

PATENT ABSTRACTS OF JAPAN

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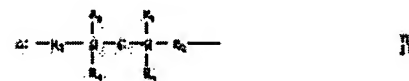
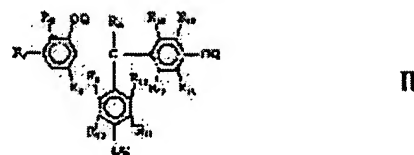
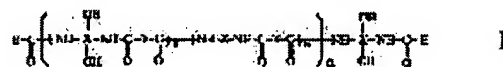
(54) POSITIVE PHOTSENSITIVE RESIN COMPOSITION AND SEMICONDUCTOR DEVICE USING SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a positive photosensitive resin composition with a high sensitivity and film endurance of a pattern and superior in adhesion to a sealing resin and storage stability by incorporating a specified polyamide and a specified photosensitive diazoquinone.

SOLUTION: This positive photosensitive resin composition comprises 100 pts.wt. of the polyamide represented by formula I and the photosensitive diazoquinone compound represented by formula II or III.

In formulae I-III, X is a tetravalent cyclic group; Y is a divalent group; Z is a group represented by formula IV; each of R1 and R2 is a divalent organic group; each of R3 and R4 is a univalent organic group; E is an aliphatic or cyclic group having at least one alkenyl or an alkynyl group; (a) is a 60-100 mol fraction; (b) is a 0-40 mol fraction; (n) is 2-500; R5 an H atom or an alkyl group; each of R6-R16 and R18-R27 is an H atom or an alkyl or alkoxy group; and Q is an H atom or the like.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

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[Date of final disposal for application]

[Patent number]

[Date of registration]

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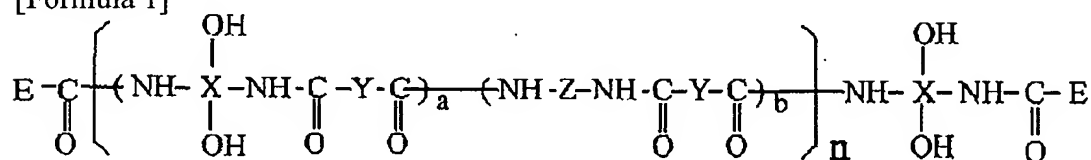
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CLAIMS

[Claim(s)]

[Claim 1] A positive type photopolymer constituent characterized by consisting of a photosensitive diazo quinone compound 1 shown by the polyamide 100 weight section, a general formula (II), or a general formula (III) shown by general formula (I) - the 100 weight sections.

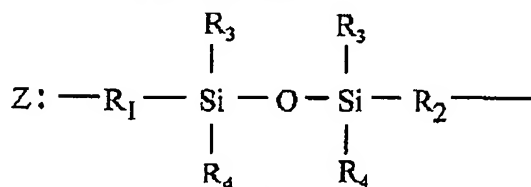
[Formula 1]



式中 X: 4価の環式化合物基

Y: 2価の環式化合物基

(I)



(R₁, R₂: 2価の有機基、R₃, R₄: 1価の有機基)

E: アルケニル基又はアルキニル基を少なくとも1個を有する
脂肪族又は環式化合物基

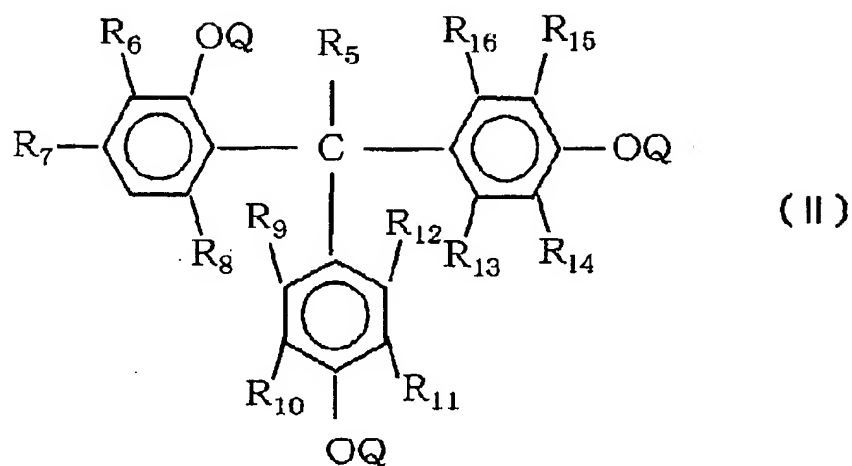
a、b はモル分率を示し、a + b = 100モル%

a = 60.0 ~ 100.0モル%

b = 0 ~ 40.0モル%

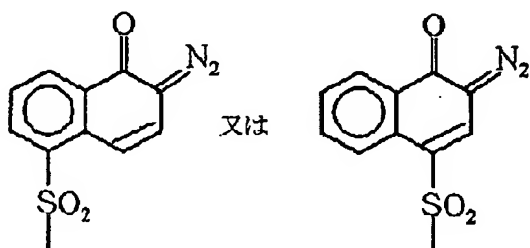
n = 2 ~ 500

[Formula 2]

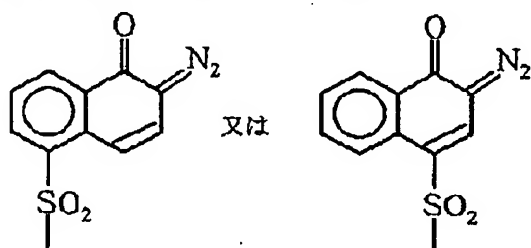


(式中、 R_5 は水素原子またはアルキル基を表し、
 $R_6, R_7, R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}, R_{14}, R_{15}, R_{16}$ はそれぞれ
 水素原子、アルキル基、アルコキシ基の内から選ばれ
 た1つを示す)

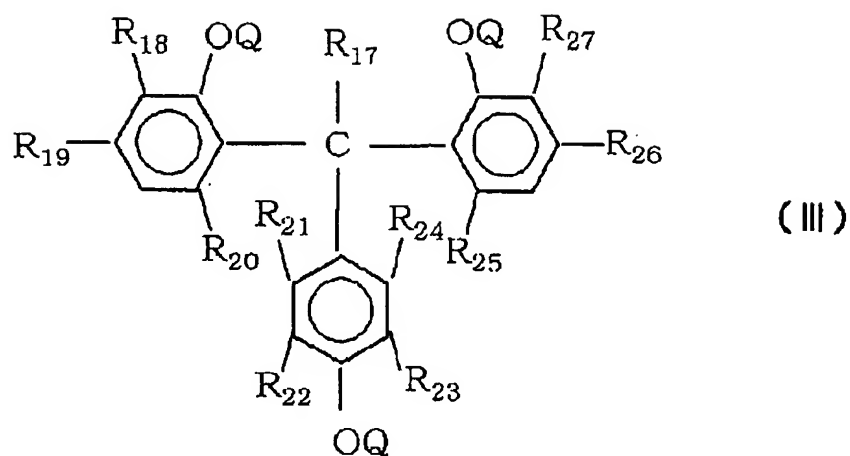
(式中Qは水素原子又は



を意味し、Qの少なくとも1つは、

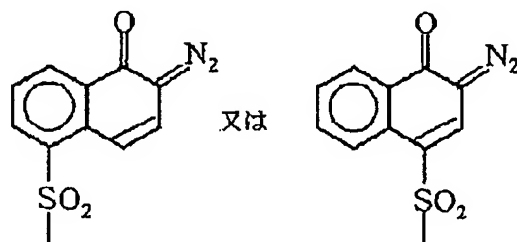


を意味する。)

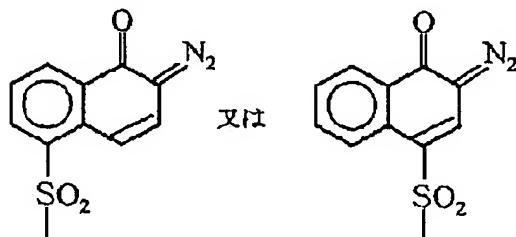


(式中、 R_{17} は水素原子またはアルキル基を表し、
 R_{18} 、 R_{19} 、 R_{20} 、 R_{21} 、 R_{22} 、 R_{23} 、 R_{24} 、 R_{25} 、 R_{26} 、 R_{27} はそれぞれ
 水素原子、アルキル基、アルコキシ基の内から選ばれた1つを示す)

(式中Qは水素原子又は



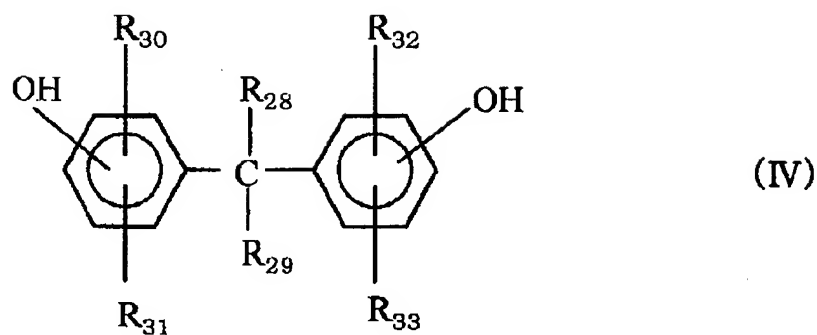
を意味し、Qの少なくとも1つは、



[Formula 3] を意味する。)

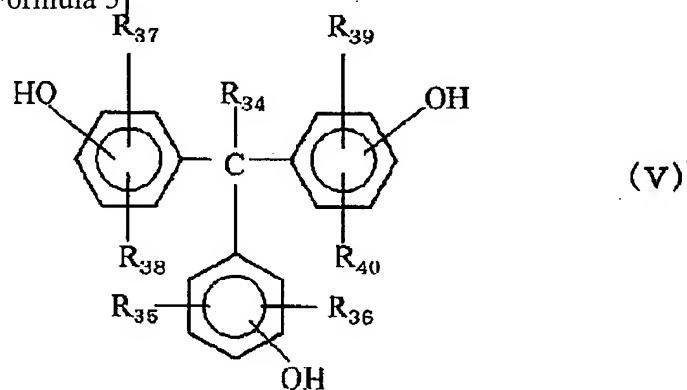
[Claim 2] A positive type photopolymer constituent characterized by consisting of the both a total of one to 30 weight section a tris phenolic compound expressed with a bisphenol compound and a general formula (V) which are expressed with a photosensitive diazo quinone compound 1 shown by the polyamide 100 weight section, a general formula (II), or a general formula (III) shown by general formula (I) - the 100 weight sections, and a general formula (IV).

[Formula 4]



(式中、 R_{28} 、 R_{29} は水素原子またはアルキル基を表し、
 R_{30} 、 R_{31} 、 R_{32} 、 R_{33} はそれぞれ水素原子、ハロゲン原子、水酸基、
 アルキル基、アルコキシ基、シクロアルキル基の内から選ばれた1つを示す)

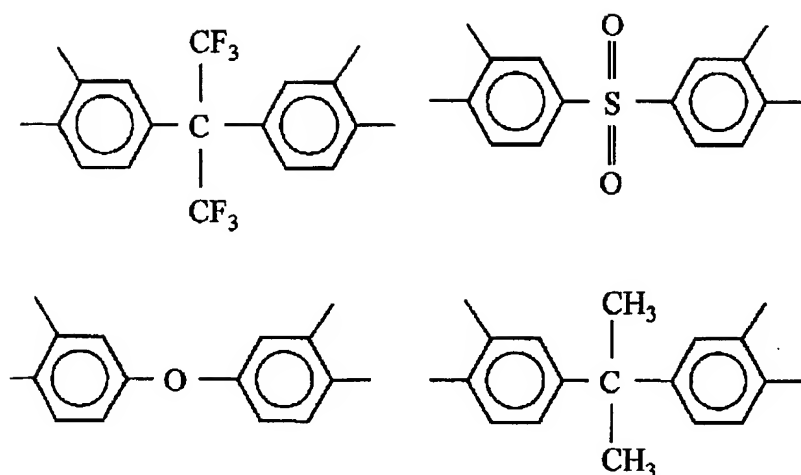
[Formula 5]



(式中、 R_{34} は水素原子またはアルキル基を表し、
 R_{35} 、 R_{36} 、 R_{37} 、 R_{38} 、 R_{39} 、 R_{40} はそれぞれ水素原子、ハロゲン原子、
 水酸基、アルキル基、アルコキシ基、シクロアルキル基の内から
 選ばれた1つを示す)

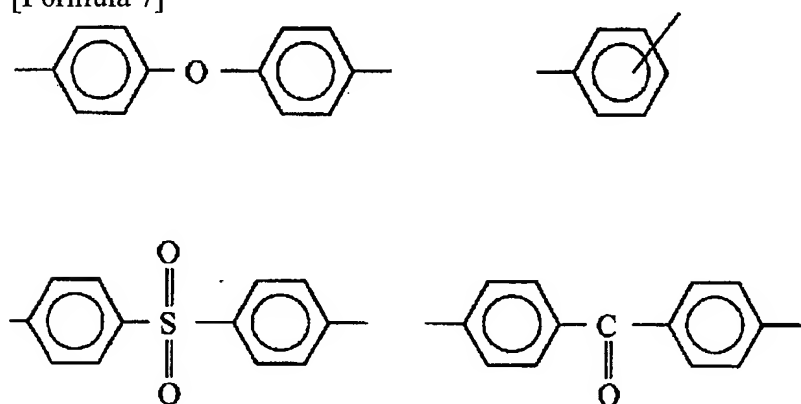
[Claim 3] A positive type photopolymer constituent according to claim 1 or 2 with which it comes to choose X in a polyamide of a general formula (I) out of the following.

[Formula 6]



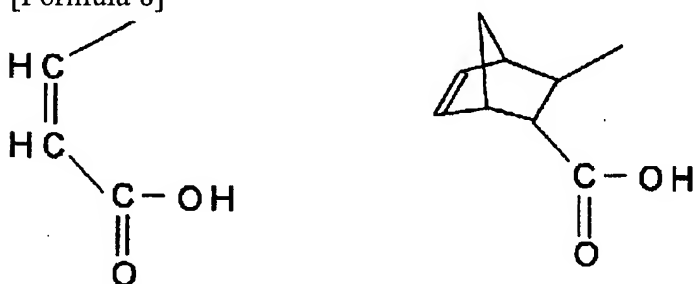
[Claim 4] A positive type photopolymer constituent according to claim 1, 2, or 3 with which it comes to choose Y in a polyamide of a general formula (I) out of the following.

[Formula 7]



[Claim 5] A positive type photopolymer constituent according to claim 1, 2, 3, or 4 with which it comes to choose E in a polyamide of a general formula (I) out of the following.

[Formula 8]



[Claim 6] A semiconductor device which prebakes, exposes, develops negatives and heats [apply on a semiconductor device and], and is obtained in a positive type photopolymer constituent according to claim 1, 2, 3, 4, or 5 so that thickness after a heating dehydration ring closure may be set to 0.1-20 micrometers.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

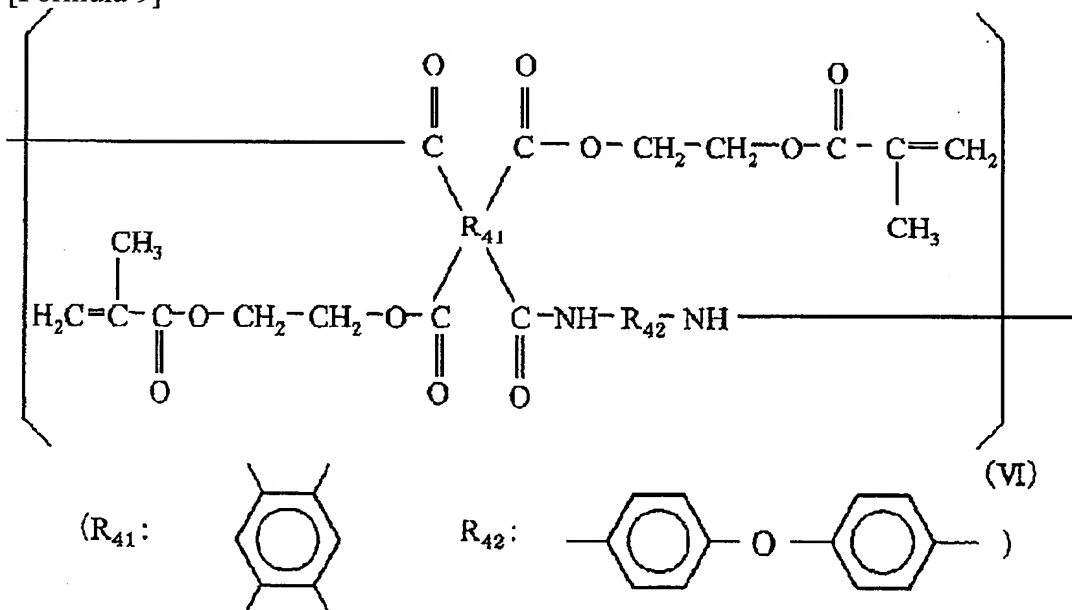
[The technical field to which invention belongs] This invention can obtain the pattern of a high remaining rate of membrane by high sensitivity, and relates to the semiconductor device using the positive type photopolymer constituent and it which are excellent in adhesion and conservation stability with closure resin.

[0002]

[Description of the Prior Art] Although the polyimide resin which has the electrical property in which thermal resistance was excellent in and excelled, a mechanical characteristic, etc. is conventionally used for the surface-protection film of a semiconductor device, and the interlayer insulation film, there is a demand of the remarkable improvement in heat-resistant cycle nature, heat-resistant shock nature, etc. in recent years by the shift to the surface mount by high integration of a semiconductor device, enlargement, thin-shape-izing of a package, a miniaturization, and the solder reflow etc., and the resin of high performance has come to be needed further. The photosensitive polyimide resin with which the technology which gives photosensitivity to polyimide resin itself attracts attention recently, for example, is shown in the following formula (VI) on the other hand is mentioned.

[0003]

[Formula 9]



[0004] When this is used, a part of pattern creation process can be simplified, there is an effect of process compaction and the improvement in the yield, but since solvents, such as a N-methyl-2-

pyrrolidone, are needed in the case of development, a problem is in safety and handling nature. Then, the photopolymer of the positive type which can do development in an alkali aqueous solution is developed recently. For example, the positive type photopolymer which consists of a poly benzo oxazole precursor and a diazo quinone compound in JP,1-46862,B is indicated. This has high thermal resistance, the outstanding electrical property, and micro-processing nature, and has not only the object for wafer coats but the possibility as resin for layer insulation. Although the diazo quinone compound of the unexposed section is insoluble in an alkali aqueous solution, when the development mechanism of the photopolymer of this positive type is exposed, a diazo quinone compound becomes meltable in a lifting and an alkali aqueous solution about a chemical change. The soluble difference of this exposure section and the unexposed section is used, and creation of the paint film pattern of only the unexposed section is attained by carrying out dissolution clearance of the exposure section. When using these photopolymers actually, it is the sensitivity of a photopolymer especially to become important. The exposure time becomes it long that it is low sensitivity, and a throughput falls. Then, if it is going to raise the sensitivity of a photopolymer and molecular weight of base resin is made small, for example, since film decrease of the unexposed section will become large at the time of development, the problem that the thickness needed is not obtained or a pattern configuration collapses arises. Moreover, when such a photopolymer is used as a surface-protection film of a semiconductor device, adhesion with the closure resin for a package fabricated at an after process on it poses especially a problem. If adhesion is bad, exfoliation will occur in the interface, and a semiconductor package carries out a crack, or water advances into the crack and it generates electric [of a semiconductor / poor]. Furthermore, an important problem is the conservation stability of a photopolymer constituent. Generally the photopolymer constituent is produced commercially in the state of the solution with base resin, a sensitization agent, and other additives. A photopolymer constituent is kept by refrigeration or refrigeration, in order to extend the expiration date. Although dry ice is put in and conveyed in case a product is conveyed, temperature falls even at -60--50 degree C in this case, a sensitization agent, an additive, etc. deposit, and it may be able to stop moreover, being able to use it.

[0005]

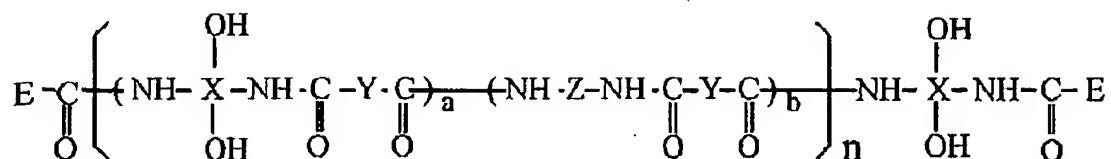
[Problem(s) to be Solved by the Invention] This invention can obtain the pattern of a high remaining rate of membrane by high sensitivity, and aims at offering the semiconductor device using the positive type photopolymer constituent and it which are excellent in adhesion and conservation stability with closure resin.

[0006]

[Means for Solving the Problem] It is the positive type photopolymer constituent characterized by this invention consisting of a photosensitive diazo quinone compound 1 shown by the polyamide 100 weight section, a general formula (II), or a general formula (III) shown by general formula (I) - the 100 weight sections. Moreover, a tris phenolic compound expressed with a bisphenol compound and a general formula (V) which are expressed with the photosensitive diazo quinone compound 1 shown by the polyamide 100 weight section, a general formula (II), or a general formula (III) shown by general formula (I) - the 100 weight sections, and a general formula (IV) It is related with a positive type photopolymer constituent characterized by consisting of the both a total of one to 30 weight section.

[0007]

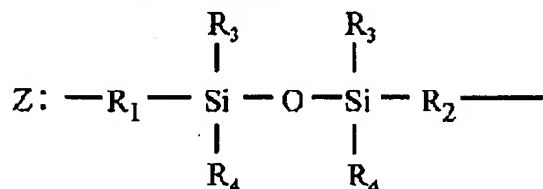
[Formula 10]



式中X:4価の環式化合物基

Y:2価の環式化合物基

(1)



(R_1, R_2 :2価の有機基、 R_3, R_4 :1価の有機基)

E:アルケニル基又はアルキニル基を少なくとも1個を有する
脂肪族又は環式化合物基

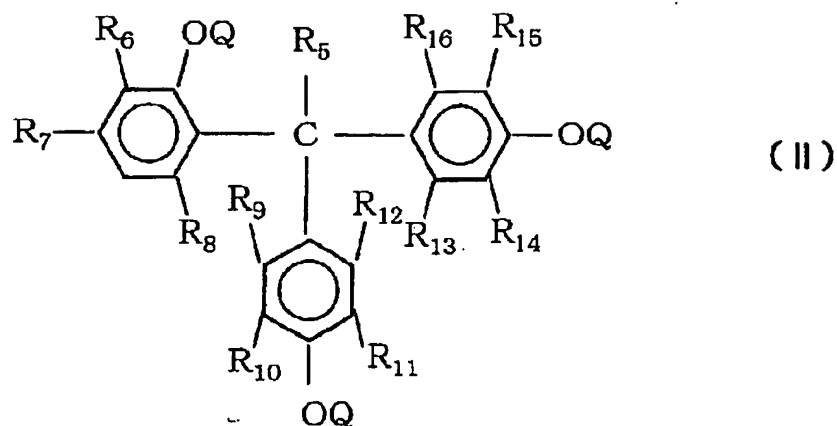
a、b はモル分率を示し、 $a+b=100$ モル%

$a=60.0 \sim 100.0$ モル%

$b=0 \sim 40.0$ モル%

$n=2 \sim 500$

[0008]



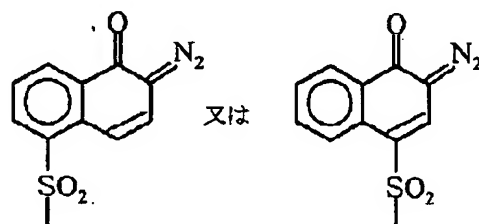
(式中、 R_5 は水素原子またはアルキル基を表し、

$R_6, R_7, R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}, R_{14}, R_{15}, R_{16}$ はそれぞれ

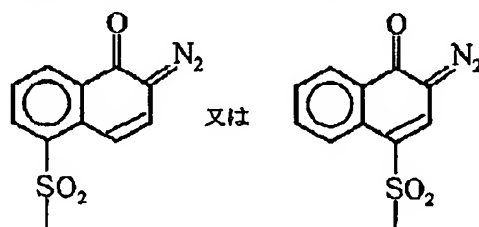
水素原子、アルキル基、アルコキシ基の内から選ばれ

た1つを示す)

(式中Qは水素原子又は



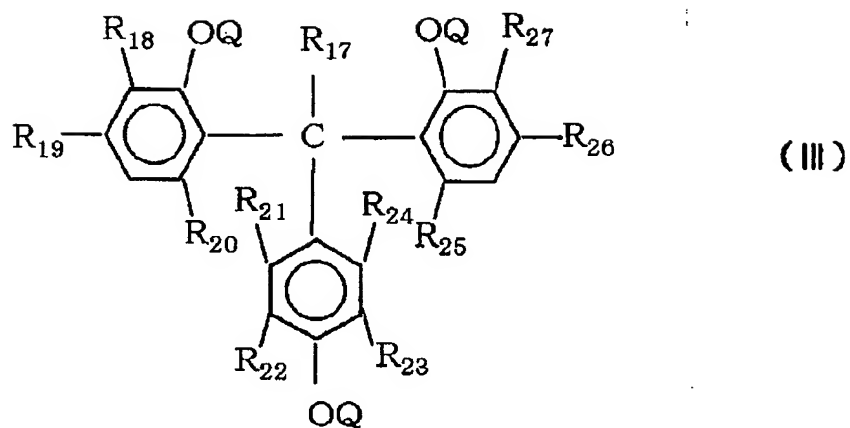
を意味し、Qの少なくとも1つは、



[Formula 11] を意味する。)

[0009]

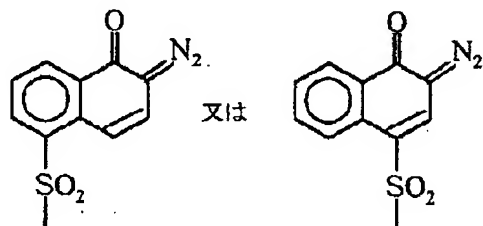
[Formula 12]



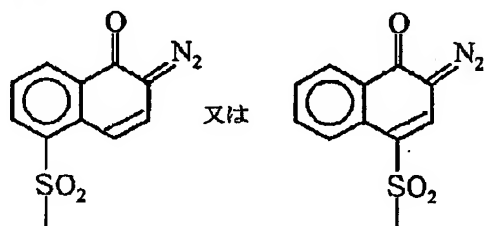
(式中、 R_{17} は水素原子またはアルキル基を表し、

R_{18} 、 R_{19} 、 R_{20} 、 R_{21} 、 R_{22} 、 R_{23} 、 R_{24} 、 R_{25} 、 R_{26} 、 R_{27} はそれぞれ水素原子、アルキル基、アルコキシ基の内から選ばれた1つを示す)

(式中Qは水素原子又は



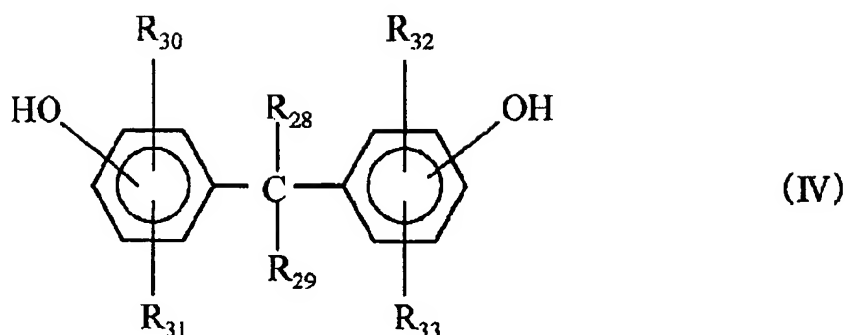
を意味し、Qの少なくとも1つは、



を意味する。)

[0010]

[Formula 13]

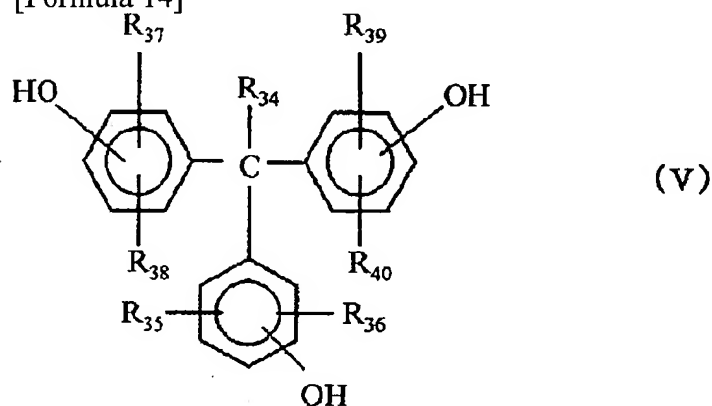


(式中、 R_{28} 、 R_{29} は水素原子またはアルキル基を表し、

R_{30} 、 R_{31} 、 R_{32} 、 R_{33} はそれぞれ水素原子、ハロゲン原子、水酸基、アルキル基、アルコキシ基、シクロアルキル基の内から選ばれた1つを示す)

[0011]

[Formula 14]

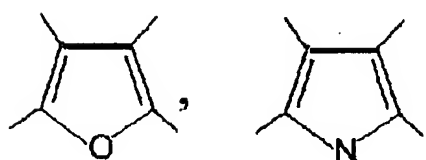
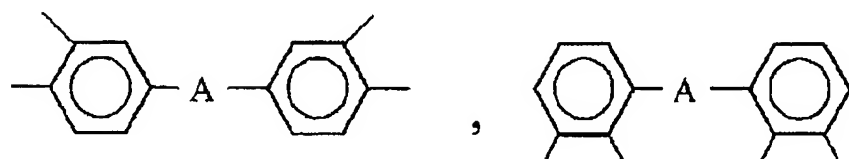
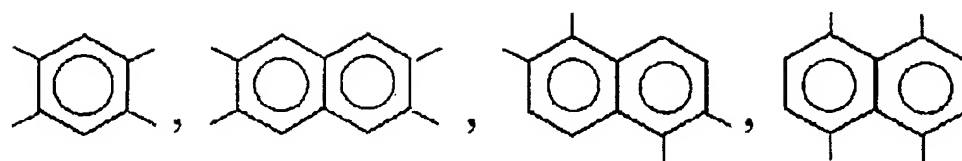


(式中、 R_{34} は水素原子またはアルキル基を表し、

R_{35} 、 R_{36} 、 R_{37} 、 R_{38} 、 R_{39} 、 R_{40} はそれぞれ水素原子、ハロゲン原子、水酸基、アルキル基、アルコキシ基、シクロアルキル基の内から選ばれた1つを示す)

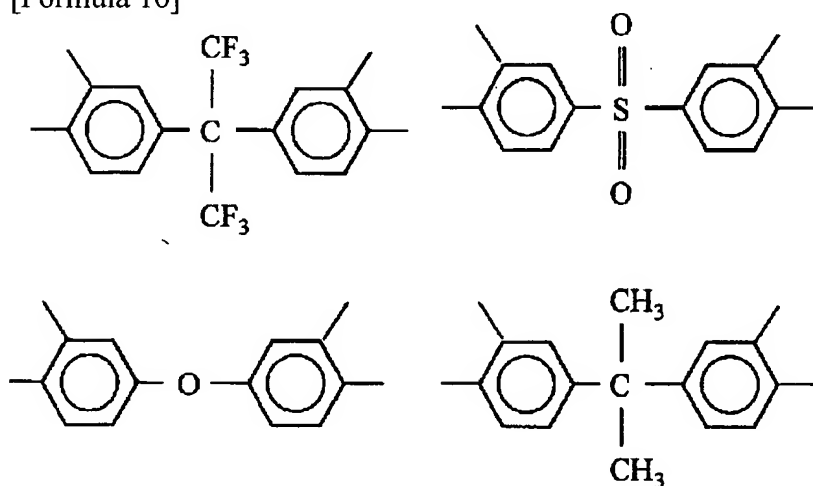
[0012] The polyamide of a formula (I) serves as a bis-aminophenol which has the structure of X, and dicarboxylic acid which has the structure of Y from the acid anhydride which has the structure of E further, if this polyamide is heated at about 300-400 degrees C, a dehydration ring closure will be carried out, and it changes to heat resistant resin called the poly benzo oxazole. X of the polyamide (I) of this invention -- for example [0013]

[Formula 15]

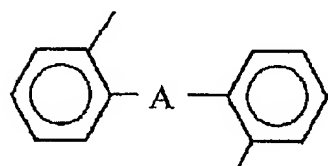
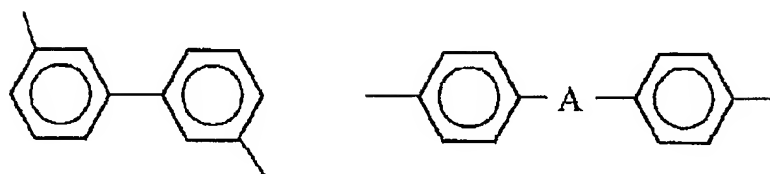
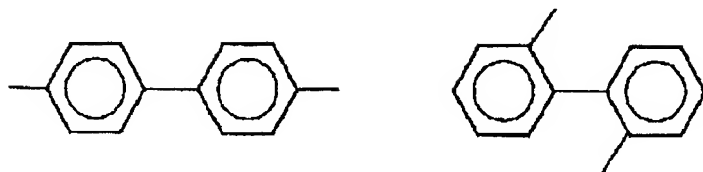
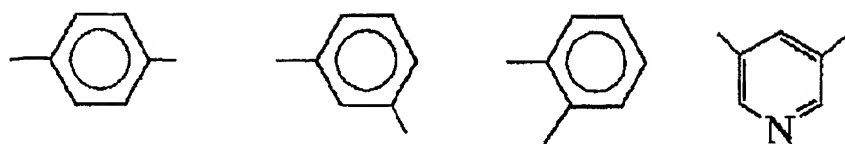


(式中A: $-\text{CH}_2-$, $-\text{C}(\text{CH}_3)_2-$, $-\text{O}-$, $-\text{S}-$, $-\text{SO}_2-$, $-\text{CO}-$,
 $-\text{NHCO}-$, $-\text{C}(\text{CF}_3)_2-$)

[0014] ***** -- although -- it is not limited to these. As a thing especially desirable in this, [0015]
 [Formula 16]

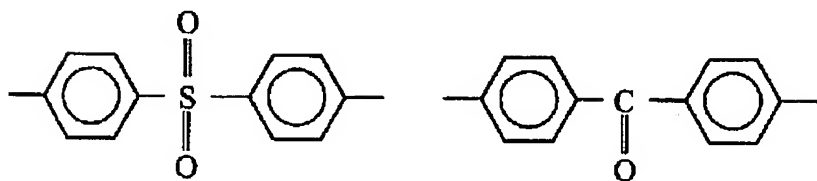
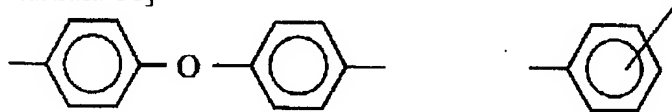


[0016] It is chosen more. Y of ***** (I) -- for example [0017]
 [Formula 17]

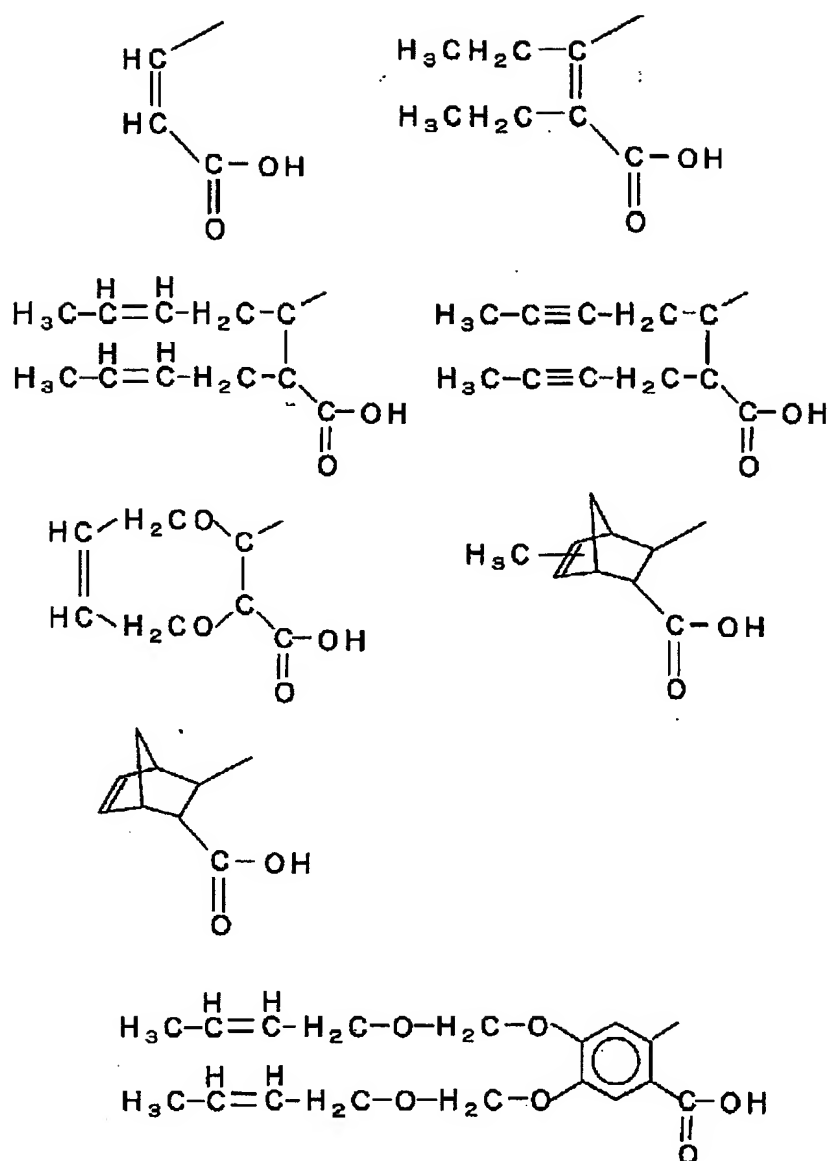


(式中A: $-\text{CH}_2-$, $-\text{C}(\text{CH}_3)_2-$, $-\text{O}-$, $-\text{S}-$, $-\text{SO}_2-$, $-\text{CO}-$,
 $-\text{NHCO}-$, $-\text{C}(\text{CF}_3)_2-$)

[0018] ***** -- although -- it is not limited to these. As a thing especially desirable in these, [0019]
 [Formula 18]

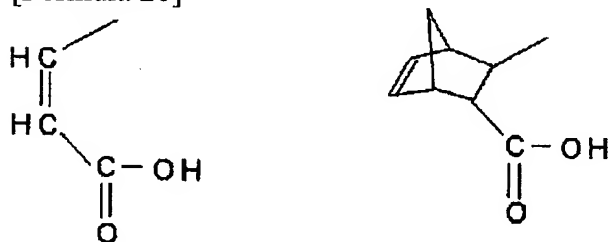


[0020] It is chosen more. E of **** (I) -- for example [0021]
 [Formula 19]



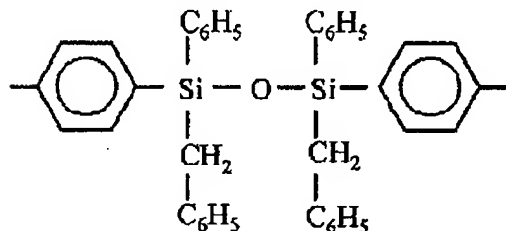
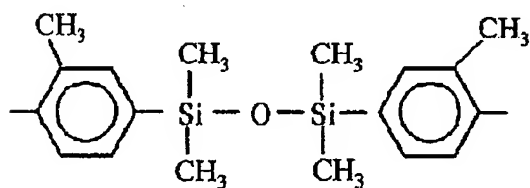
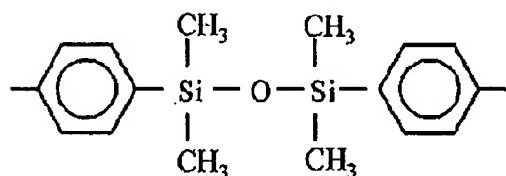
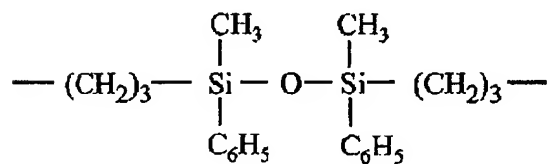
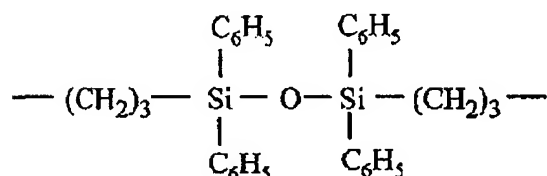
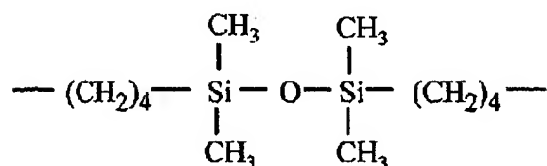
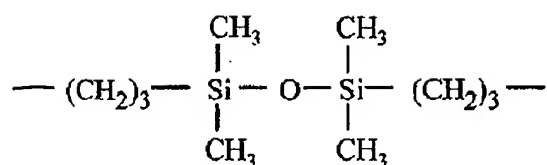
[0022] Although ** is mentioned, it is not limited to these. As a thing especially desirable in this, [0023]

[Formula 20]



[0024] It is chosen more. After this invention makes the dicarboxylic acid derivative which has the structure of Y, and the bis-aminophenol which has the structure of X react and compounds a polyamide, it caps the amino group of an end using the acid anhydride which has the alkenyl radical or at least one alkynyl group shown in E of a formula (I). furthermore, Z of a formula (I) -- for example [0025]

[Formula 21]



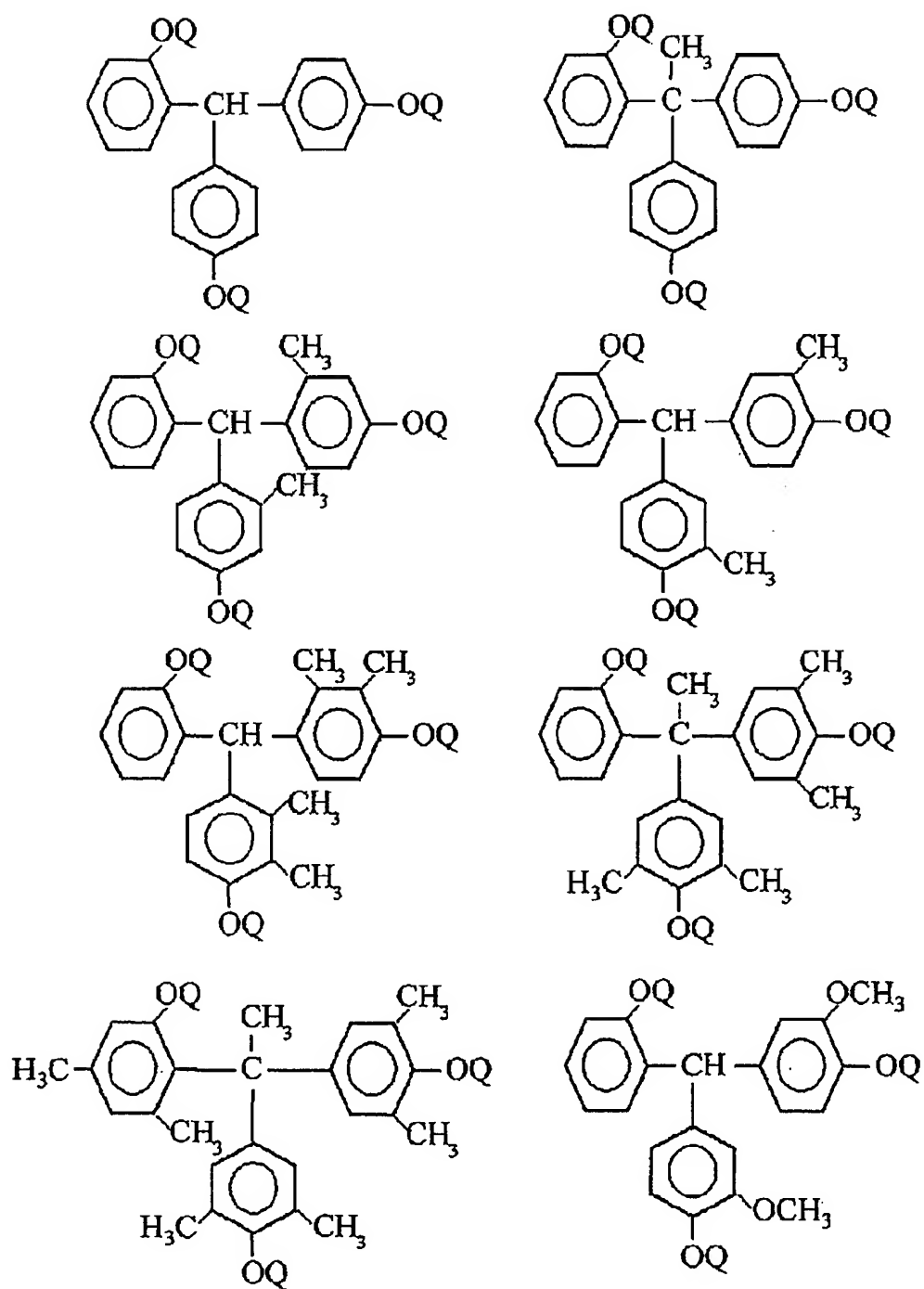
[0026] ***** -- although -- it is not limited to these. Although especially Z of a formula (1) is used to a substrate like a silicon wafer when the outstanding adhesion is required, the operating rate b is to a maximum of 40.0-mol %. If 40.0-mol % is exceeded, the solubility of resin will fall extremely, the development remainder (Society for Cutting Up Men) occurs, and pattern processing cannot be performed. In addition, in an activity of these X, Y, E, and Z, it does not matter even if it is one kind, respectively and is two or more kinds of mixture.

[0027] The photosensitive diazo quinone compound used by this invention is a reactant of the compound

which has 1 and 2-benzoquinone diazido or 1, and 2-naphthoquinonediazide structure, and the phenol system compound which is a base material. Especially in the positive type photopolymer constituent of this invention, it is the object which obtains high sensitivity and a high remaining rate of membrane at the time of development, and it is important to add to a presentation the photosensitive diazo quinone compound which has the structure shown by the general formula (II) or the general formula (III). When the soluble difference of the exposure section and the unexposed section is used as the development mechanism of the photopolymer of a positive type was mentioned above, and it is going to obtain high sensitivity and a high remaining rate of membrane, in order to enlarge the difference, the exposure section tends to melt, and the unexposed section needs to change solubility so that it may be harder to melt and may become. Change of the soluble difference has the large place based also on the structure of the phenol system compound which is a base material. Then, the result of having looked for the photosensitive diazo quinone compound which has the base material which can promote solubility in the exposure section at the time of development, and the lysis inhibition effect can be helped [base material] in the unexposed section, and can make sufficient remaining rate of membrane holding, Adjust the molecular weight of a support phenol system compound, and the aromatic series radical which has a hydroxyl group is arranged uniformly moderately. And it found out that the photosensitive diazo quinone compound which used as the base material the phenol system compound with the structure where it has at least one aromatic series radical which has not replaced the para position to a hydroxyl group was excellent. Furthermore, this photosensitive diazo quinone compound found out that the direction combined with the poly benzo oxazole precursor discovered a high remaining rate of membrane while the twist combined with a polyimide precursor also maintains high sensitivity. As a photosensitive diazo quinone compound shown in a general formula (II), although the following etc. are mentioned, it is not limited to these.

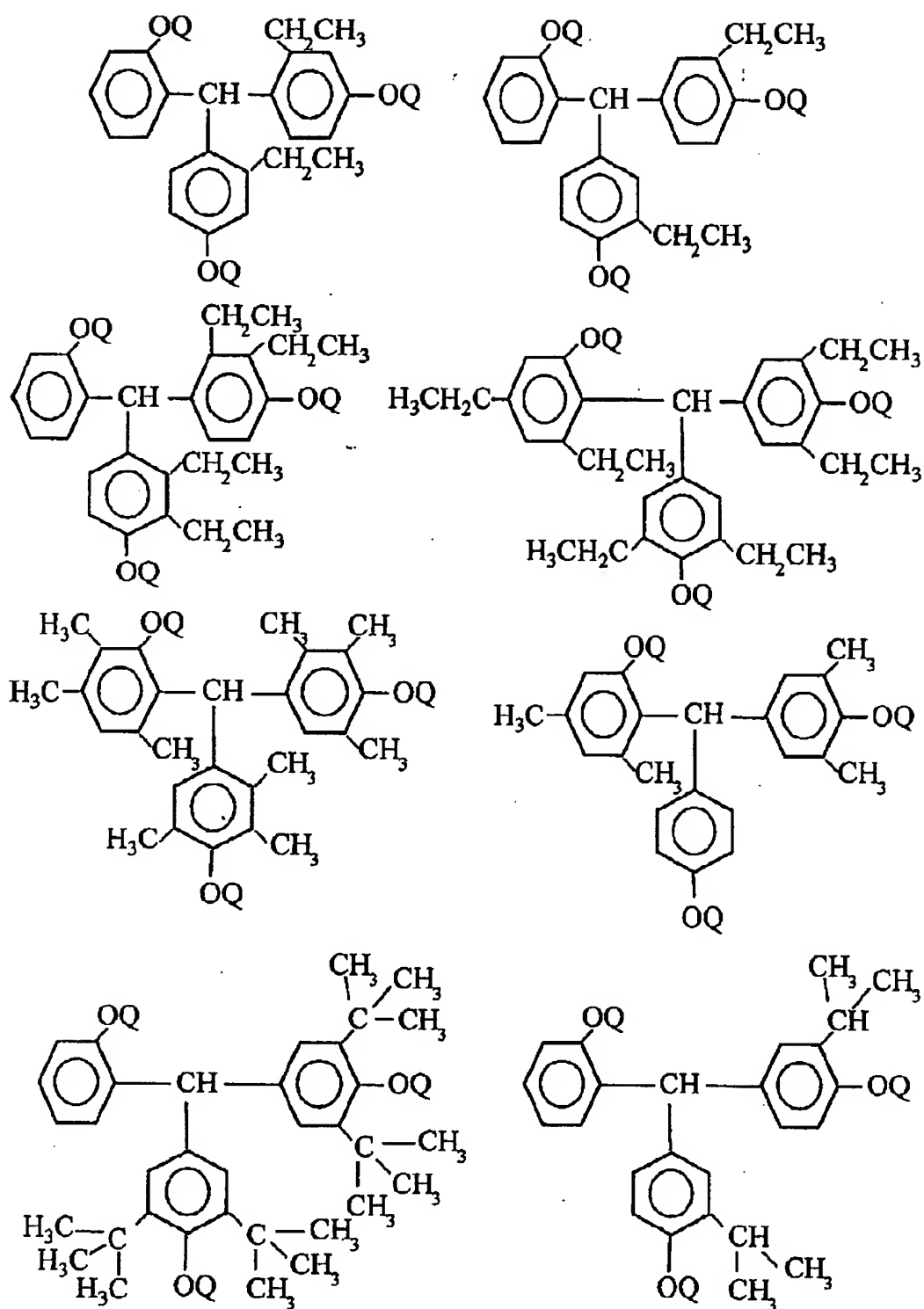
[0028]

[Formula 22]



[0029]

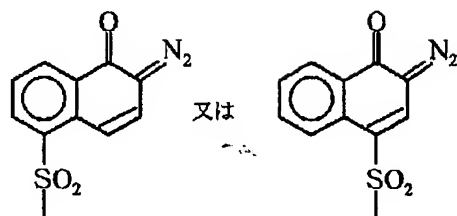
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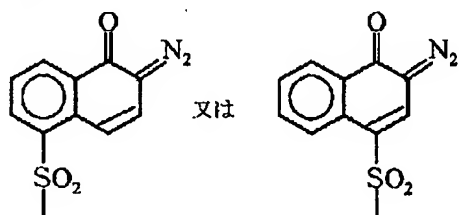
[0030]

[Formula 24]

(式中Qは水素原子又は



を意味し、Qの少なくとも1つは、

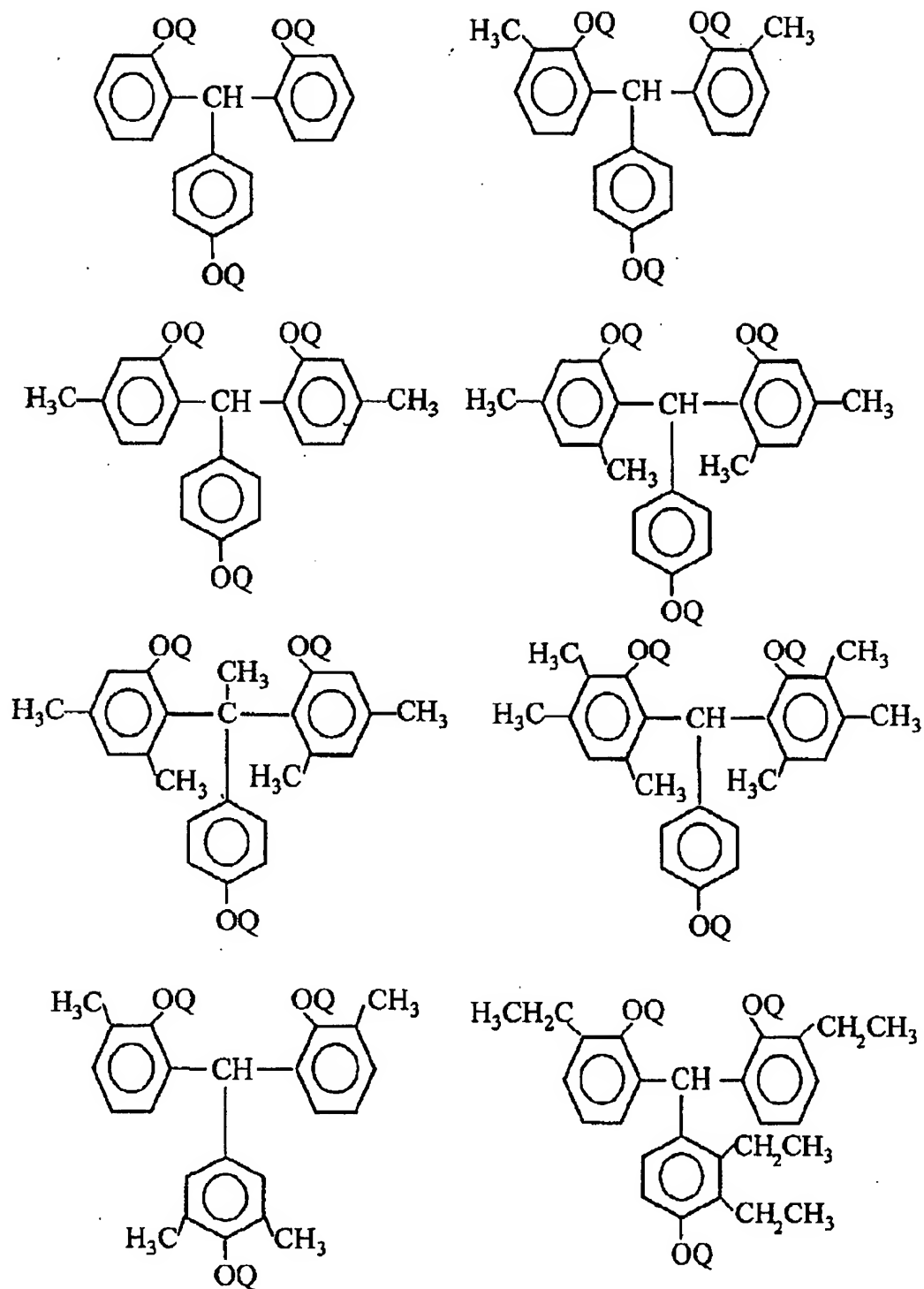


を意味する。)

[0031] As a photosensitive diazo quinone compound shown in a general formula (III), although the following etc. are mentioned, it is not limited to these.

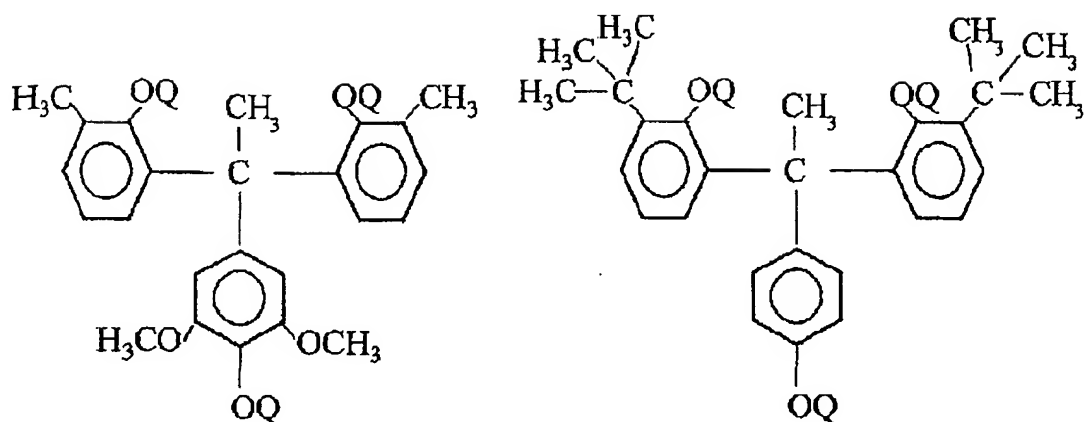
[0032]

[Formula 25]



[0033]

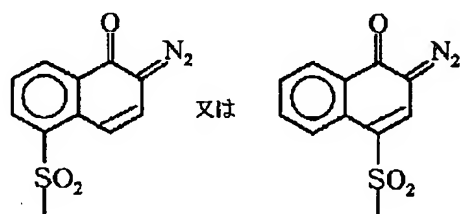
[Formula 26]



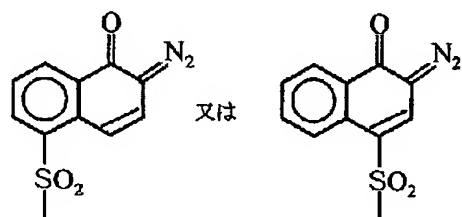
[0034]

[Formula 27]

(式中Qは水素原子又は



を意味し、Qの少なくとも1つは、

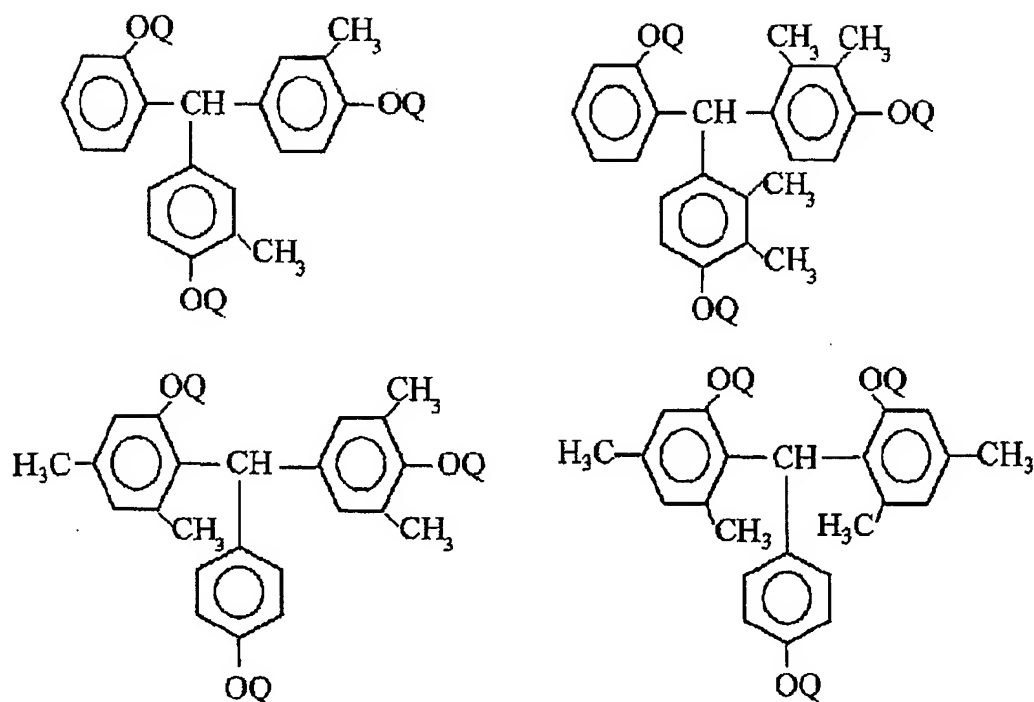


を意味する。)

[0035] The following are desirable from the point of high sensitivity and a high remaining rate of membrane especially in these.

[0036]

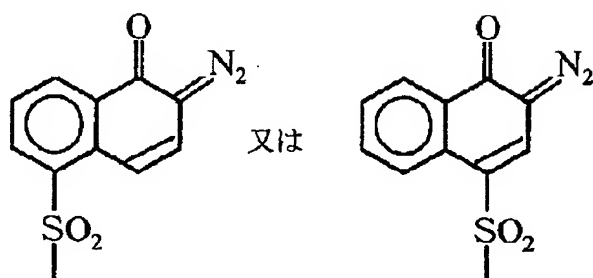
[Formula 28]



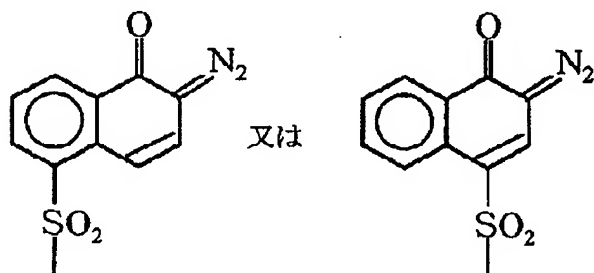
[0037]

[Formula 29]

(式中Qは水素原子又は



を意味し、Qの少なくとも1つは、



を意味する。)

[0038] Moreover, if the loadings to the polyamide of a photosensitive diazo quinone compound are the 1 - 100 weight section, its patterning nature of resin is poor if loadings are under 1 weight section, and they exceed the 100 weight sections conversely to the polyamide 100 weight section, not only sensitivity

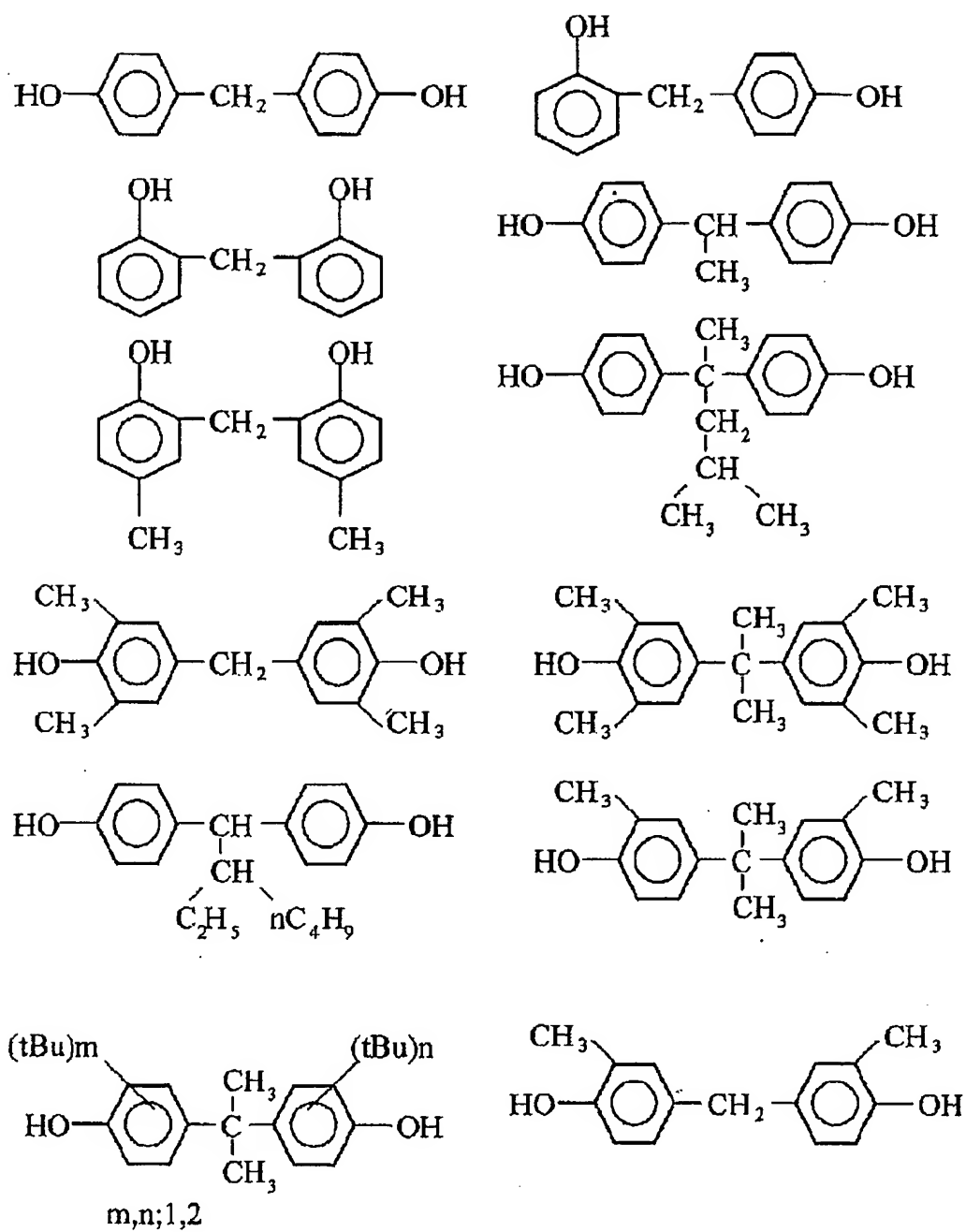
falls substantially, but the tension pace of expansion of a film will fall remarkably.

[0039] In order to raise a sensitization property as occasion demands, a dihydropyridine derivative can be added to the positive type photopolymer constituent of this invention. As a dihydropyridine derivative, for example 2, the 6-dimethyl -3, 5-diacetyl-4-(2'-nitrophenyl)-1, a 4-dihydropyridine, 4-(2'-nitrophenyl)-2, the 6-dimethyl -3, 5-JIKARUBO ethoxy -1, a 4-dihydropyridine, 4-(2' and 4'-dinitrophenyl)-2, the 6-dimethyl -3, 5-JIKARUBO methoxy -1, a 4-dihydropyridine, etc. can be mentioned.

[0040] It is important to use together the tris phenolic compound shown by the bisphenol compound further shown by the general formula (IV) in the positive type photopolymer constituent of this invention and the general formula (V). If the phenolic compounds shown by these general formulas (IV) and the general formula (V) are added to the positive type photopolymer presentation which consists of a poly benzo oxazole precursor and a diazo quinone compound, even if adhesion with closure resin will improve, and high sensitivity and a high remaining rate of membrane will be further obtained at the time of development and it will keep it at the low temperature which is -60--50 degree C, the positive type photopolymer constituent which does not have a deposit of a phenol etc. and was excellent in shelf life is obtained. Although it is also effective that the adhesion with closure resin adds independently the phenolic compounds shown by the general formula (IV) and the general formula (V) as for a degree, if the bisphenol compound shown by the general formula (IV) when an addition is increased independently, respectively is kept at -60--50 degree C low temperature, a deposit will become easy to take place. Moreover, decline in a remaining rate of membrane with the remarkable tris phenolic compound shown by the general formula (V) is seen. However, by using together the tris phenolic compound shown by the bisphenol compound shown by the general formula (IV), and the general formula (V), the defect which each has has been improved and the outstanding adhesion of the sensitization property of high sensitivity and closure resin was also discovered further. The addition of phenolic compounds is the both a total of one to 30 weight section about the tris phenolic compound expressed with the bisphenol compound expressed with a general formula (IV), and a general formula (V) to the polyamide 100 weight section shown by the general formula (I). If there are more additions of both phenolic compounds than 30 weight sections, a deposit will arise in low-temperature storage of -60--50 degree C as mentioned above, or the remarkable decline in a remaining rate of membrane will take place at the time of development. The sensitivity at the time of about [that adhesion with closure resin falls / an addition / under in 1 weight section] or development falls. Although the following etc. can be mentioned as a bisphenol compound shown in a general formula (IV), it is not limited to these.

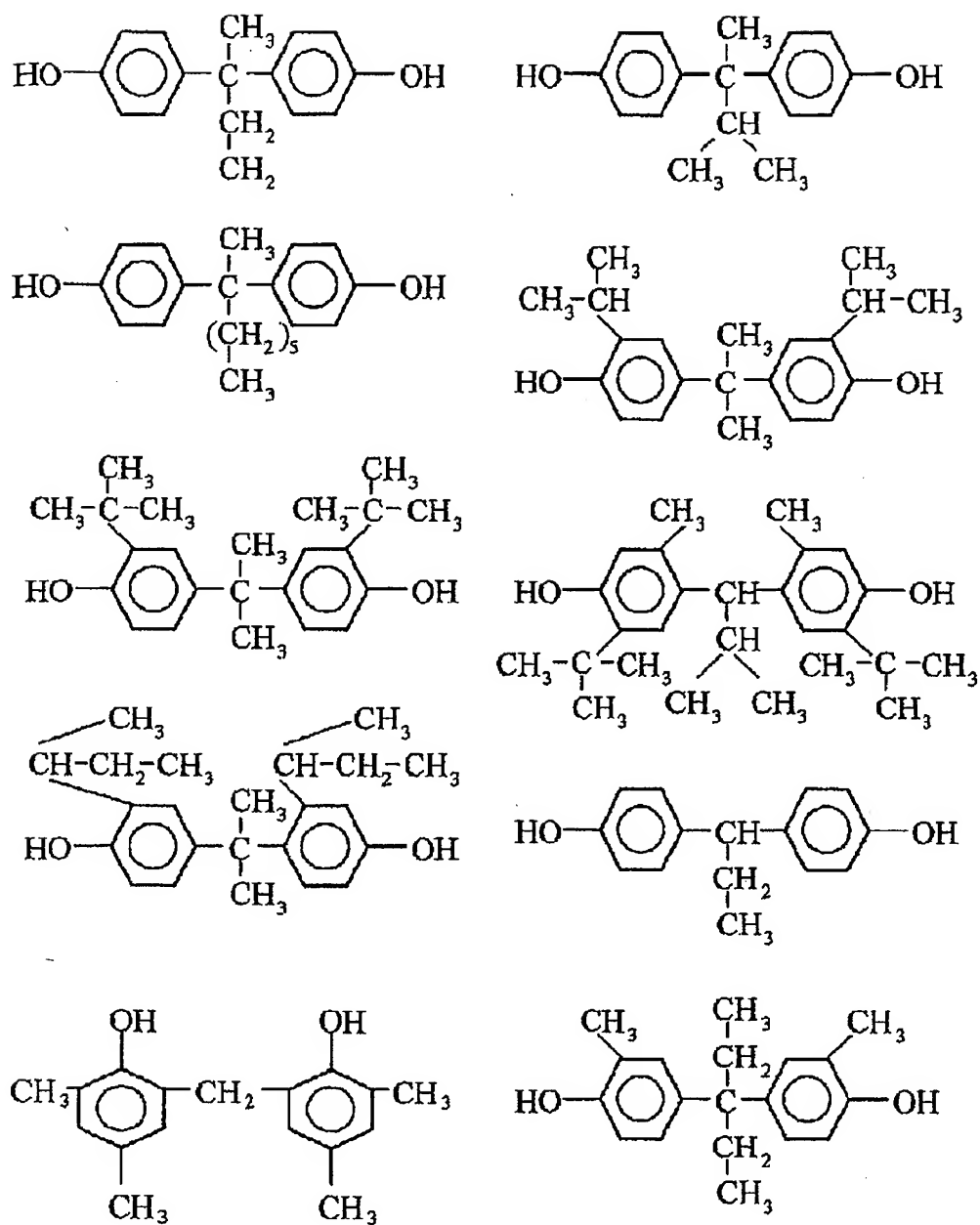
[0041]

[Formula 30]



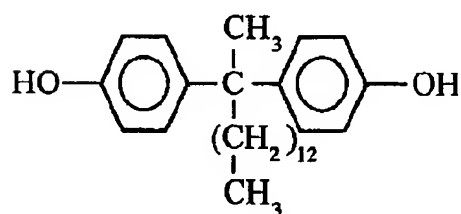
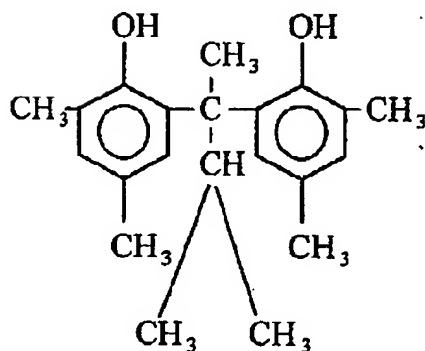
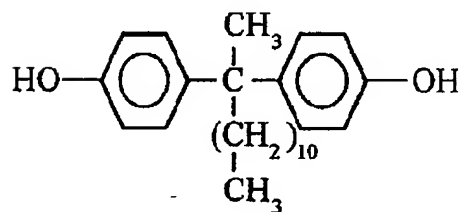
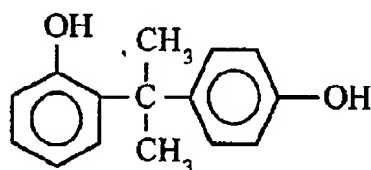
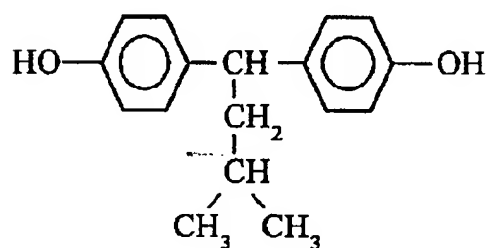
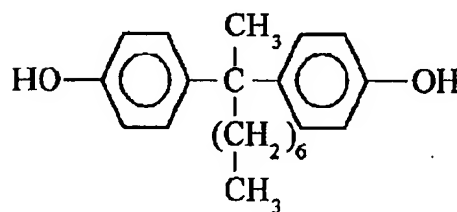
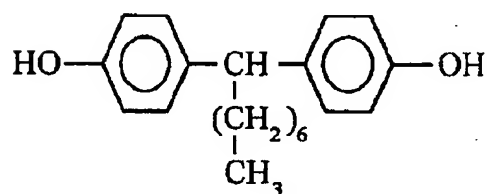
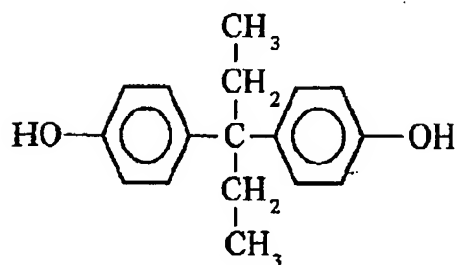
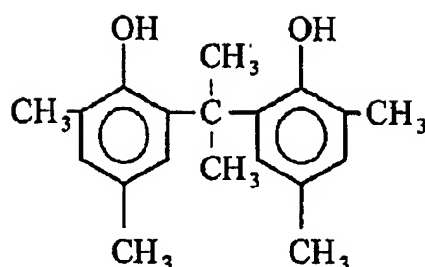
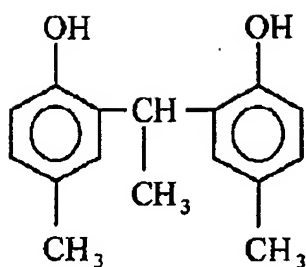
[0042]

[Formula 31]

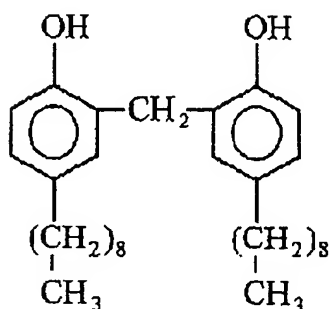
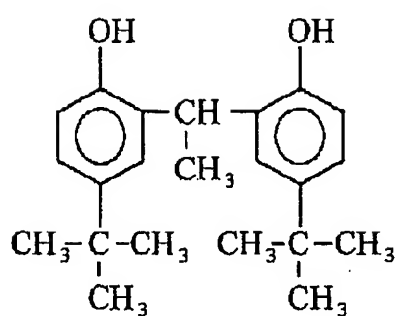
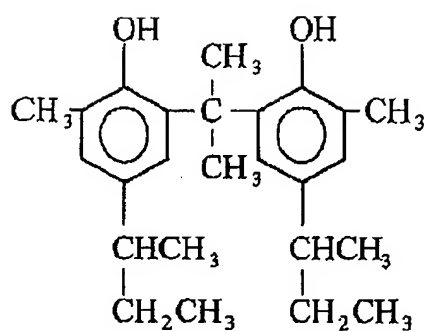


[0043]

[Formula 32]

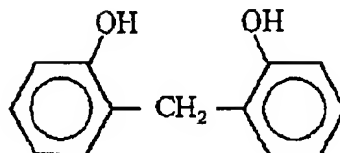
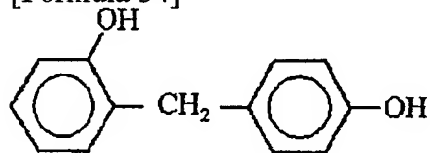


[0044]
[Formula 33]



[0045] As a thing especially desirable in these, [0046]

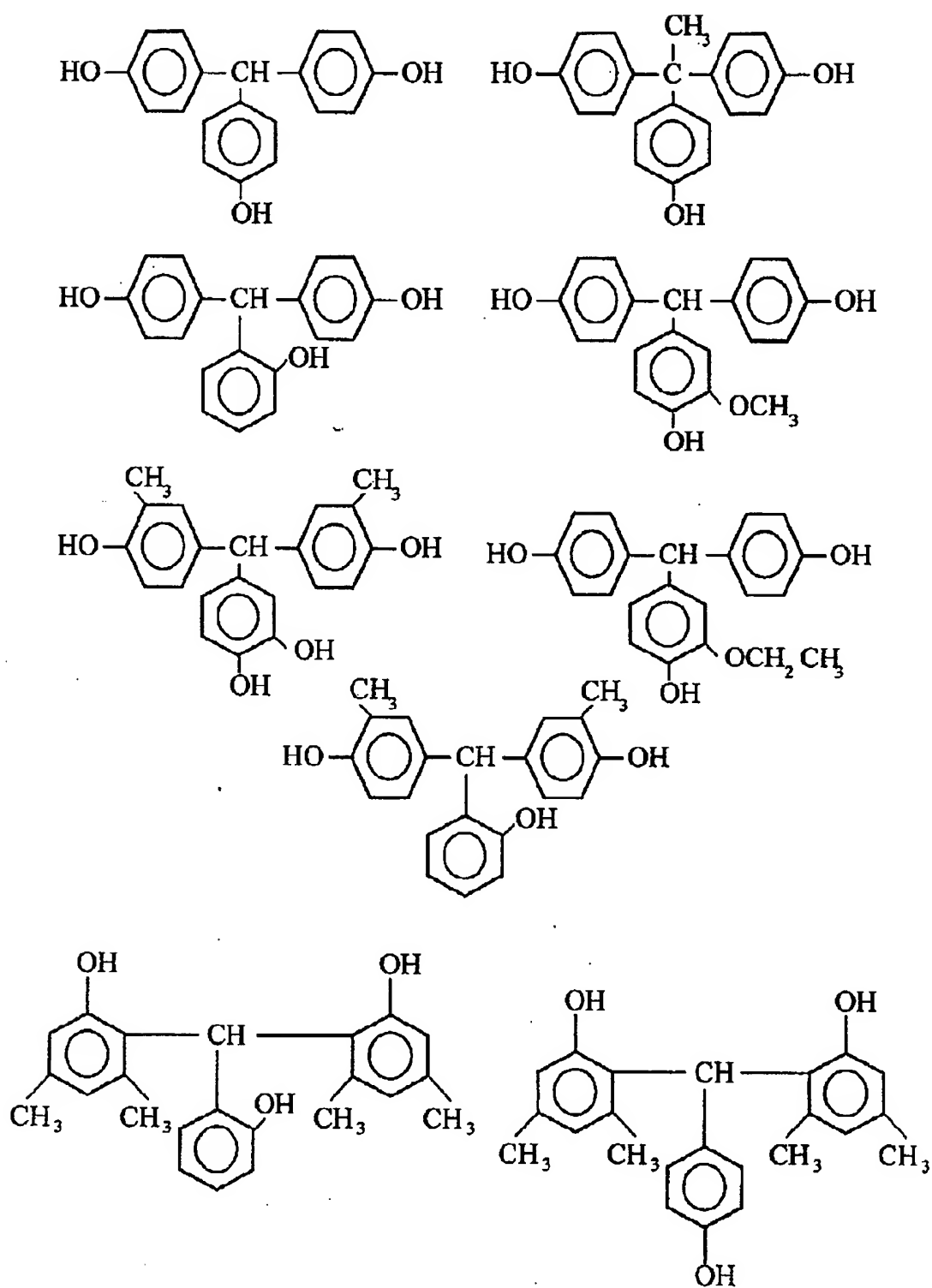
[Formula 34]



[0047] It comes out. Moreover, although the following etc. can be mentioned as a compound shown in a general formula (V), it is not limited to these.

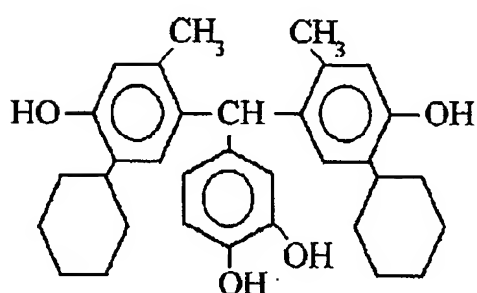
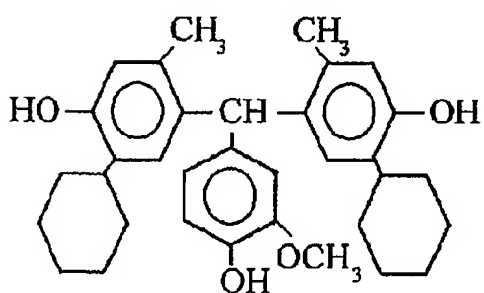
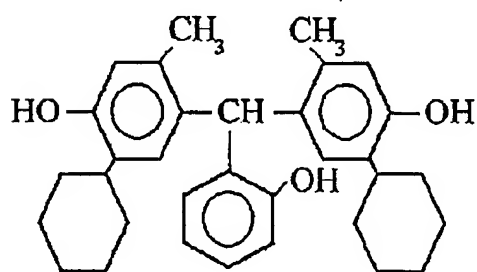
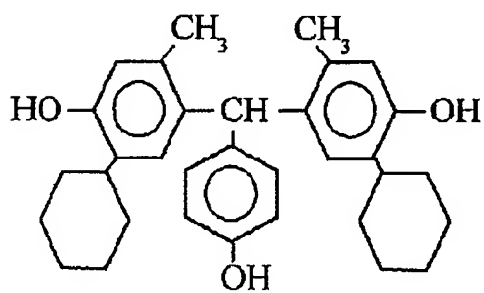
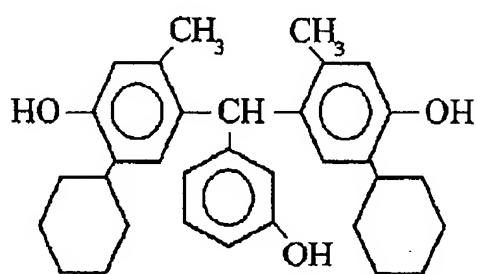
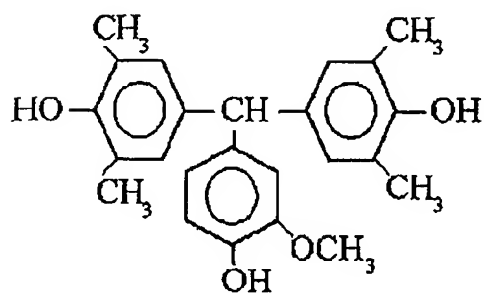
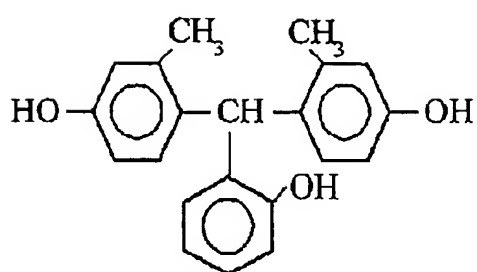
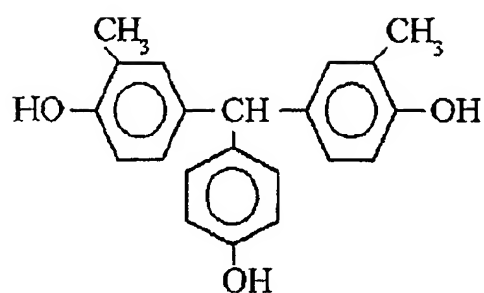
[0048]

[Formula 35]

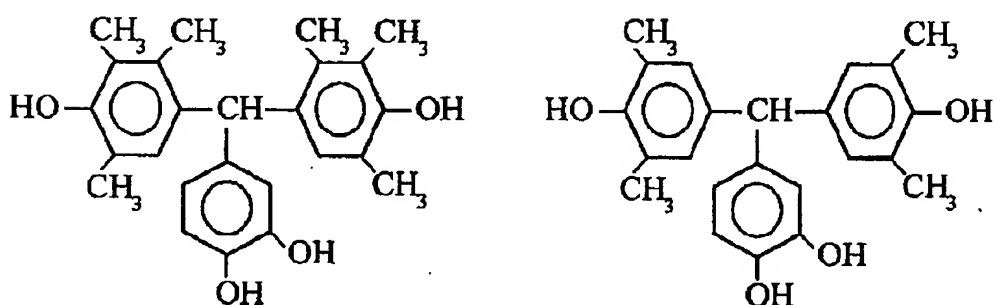
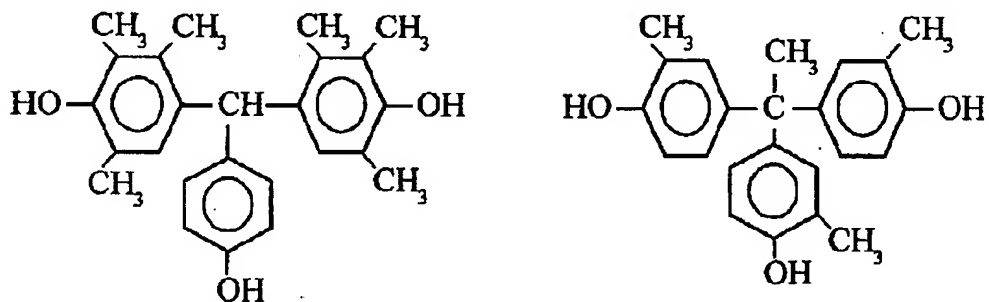
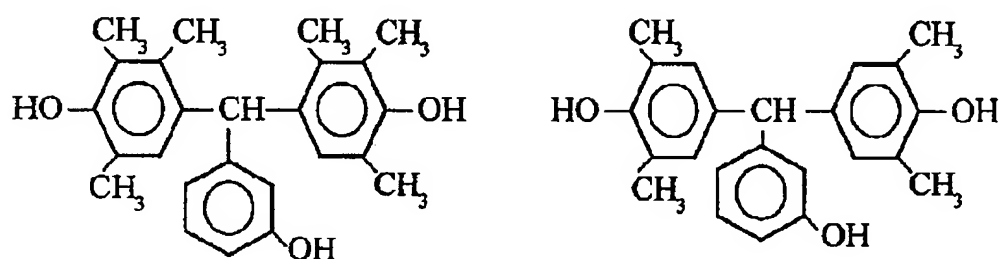
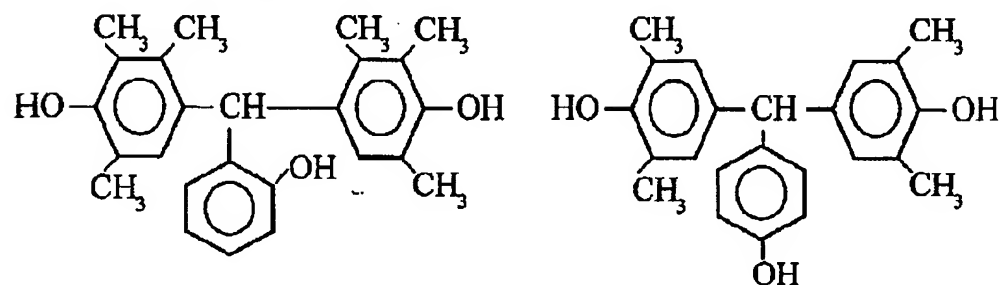
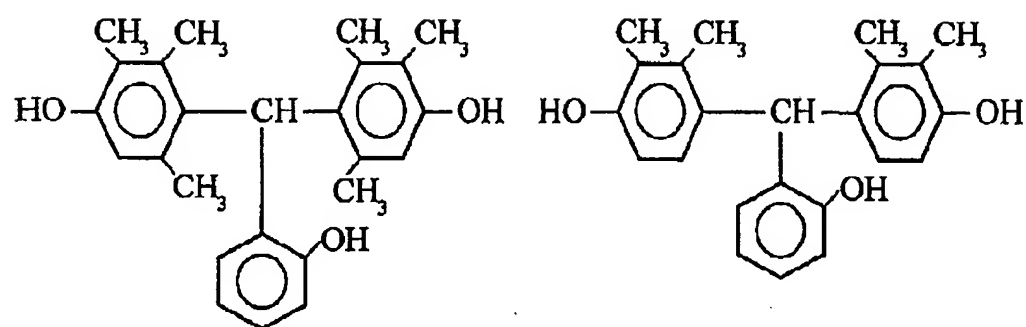


[0049]

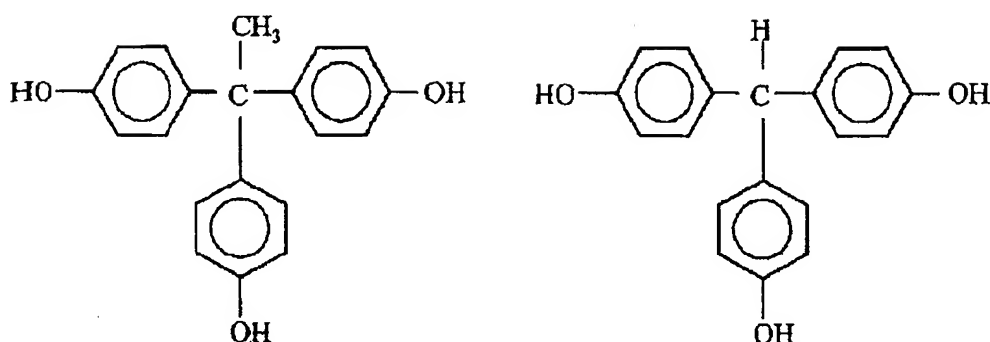
[Formula 36]



[0050]
[Formula 37]



[0051] As a thing especially desirable in these, [0052]
[Formula 38]



[0053] It comes out. In the positive type photopolymer constituent in this invention, additives, such as a leveling agent and a silane coupling agent, can be added as occasion demands. In this invention, these components are dissolved in a solvent, and it is used by making it the shape of a varnish. As a solvent, a N-methyl-2-pyrrolidone, gamma-butyrolactone, N,N-dimethylacetamide, dimethyl sulfoxide, diethylene-glycol wood ether, Diethylene-glycol diethylether, diethylene-glycol dibutyl ether, Propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, Propylene-glycol-monomethyl-ether acetate, methyl lactate, Ethyl lactate, butyl lactate, methyl -1, 3-butylene-glycol acetate, 1, the 3-butylene-glycol-3-monomethyl ether, methyl pyruvate, pyruvic-acid ethyl, methyl-3-methoxy propionate, etc. are mentioned, and it may be independent, or you may mix and use.

[0054] The operation of the positive type photopolymer constituent of this invention applies this constituent to a suitable base material, for example, a silicon wafer, a ceramic substrate, an aluminum substrate, etc. first. In the case of a semiconductor device, coverage is applied so that the last thickness after hardening may be set to 0.1-20 micrometers. It becomes difficult to fully demonstrate the function as a protection membrane surface of a semiconductor device as thickness is 0.1 micrometers or less and it not only becomes difficult to obtain a detailed processing pattern as it is 20 micrometers or more, but processing takes time amount and a throughput falls. There are revolution spreading using the spinner as the method of application, fuel-spray spreading using a spray coater, immersion, printing, roll coating, etc. Next, it prebakes at 60-130 degrees C, and chemical rays are irradiated after drying a paint film at a desired pattern configuration. As chemical rays, although an X-ray, an electron ray, ultraviolet rays, a visible ray, etc. can be used, a thing with a wavelength of 200-500nm is desirable. Next, a relief pattern is obtained by carrying out dissolution clearance of the exposure section with a developer. As a developer, a sodium hydroxide, a potassium hydroxide, a sodium carbonate, Inorganic alkali, such as a sodium silicate, a meta-sodium silicate, and aqueous ammonia Primary amine, such as ethylamine and n propylamine, diethylamine, The 3rd amines, such as the 2nd amines, such as G n propylamine, triethylamine, and methyl diethylamine, Alcoholic amines, such as dimethylethanolamine and triethanolamine, The aqueous solution of alkali, such as quarternary ammonium salt, such as tetramethylammonium hydroxide and tetraethylammonium hydroxide, And the aqueous solution which carried out suitable amount addition of the water-soluble organic solvents and surfactants like a methanol and ethanol, such as alcohols, can be suitably used for this. As the development method, methods, such as a spray, a paddle, immersion, and an ultrasonic wave, are possible. Next, the rinse of the relief pattern formed by development is carried out. Distilled water is used as a rinse. Next, it heat-treats, an oxazole ring is formed and the last pattern which is rich in thermal resistance is obtained. The positive type photopolymer constituent by this invention is useful also as the layer insulation of not only a semiconductor use but a multilayer circuit, the cover coat of a flexible copper-clad sheet, a solder resist film, a liquid crystal orientation film, etc.

[0055]

[Example] Hereafter, an example explains this invention concretely.

<<example 1>>

* The synthetic diphenyl ether -4, one mol of 4'-dicarboxylic acid, 1-hydroxy of a polyamide - 1, 2, two mols of 3-benzotriazols 443.2g (0.9 mols) of dicarboxylic acid derivatives, hexafluoro which were made

to react and were obtained - 2 and 2-screw (3-amino-4-hydroxyphenyl) propane 366.3g (1.0 mols) is put into the separable flask of a thermometer, an agitator, raw material input port, and 4 openings equipped with the desiccation nitrogen gas installation pipe, and 3000g of N-methyl-2-pyrrolidones was added, and it was made to dissolve. It was made to react at 75 degrees C for 12 hours using an oil bath after that. Next, the 5-norbornene -2 and 32.8g (0.2 mols) of 3-dicarboxylic acid anhydrides dissolved in 500g of N-methyl-2-pyrrolidones were added, it stirred for further 12 hours, and the reaction was ended. After carrying out the ** collection of the charge and the precipitate to the solution of water / methanol =3/1 and washing the reaction mixture after filtering a reaction mixture enough with water, it dried under the vacuum and the target polyamide (A-1) was obtained.

[0056] * After dissolving polyamide (A-1) 100g in which the positive type photopolymer constituent carried out production composition, and diazo quinone (B-1) 25g which has the structure of the following formula in 250g of N-methyl-2-pyrrolidones, it filtered with the 0.2-micrometer Teflon filter, and the photopolymer constituent was obtained.

[0057] * After using the spin coater and applying the positive type photopolymer constituent of ***** on a silicon wafer, it was dried at 120 degrees C with the hot plate for 4 minutes, and the paint film of about 5 micrometers of thickness was obtained. g line stepper exposure machine NSR-1505 G3A (NIKON CORP. make) increased 10 mJ/cm every 2 from 50 mJ/cm² through reticle to this paint film, and it exposed to 540 mJ/cm². Next, after carrying out dissolution clearance of the exposure section by being immersed in 1.40% of tetramethylammonium hydroxide aqueous solution for 60 seconds, the rinse was carried out for 30 seconds with pure water. Consequently, it has checked that the pattern was fabricated from the portion irradiated by light exposure 230 mJ/cm². (Sensitivity is 230 mJ/cm²). The remaining rate of membrane at this time (thickness x100 before the thickness/development after development) showed 93.1% and a very high value.

[0058] <<example 2>> Set to composition of the polyamide in an example 1. Diphenyl ether -4, one mol of 4'-dicarboxylic acid, 1-hydroxy - instead of the dicarboxylic acid derivative which two mols of 1, 2, and 3-benzotriazols were made to react, and was obtained Diphenylsulfone -4, one mol of 4'-dicarboxylic acid, 1-hydroxy - Compounding the polyamide (A-2) using the dicarboxylic acid derivative which two mols of 1, 2, and 3-benzotriazols were made to react, and was obtained, others performed the same assessment as an example 1.

<<example 3>> It sets to composition of the polyamide in an example 1, and is hexafluoro. - 3, the 3'-diamino -4, and 4'-dihydroxy diphenylsulfone were used instead of 2 and 2-screw (3-amino-4-hydroxyphenyl) propane, the polyamide (A-3) was compounded, and others performed the same assessment as an example 1.

<<example 4>> In composition of the polyamide in an example 1, the maleic anhydride was used instead of 5-norbornene -2 and 3-dicarboxylic acid anhydride, the polyamide (A-4) was compounded, and others performed the same assessment as an example 1.

<<example 5>> Changed the photosensitive diazo quinone compound B-1 in the photopolymer constituent in an example 1 to B-2, further, the addition of this component was changed, as shown in a table 1, and also the same assessment as an example 1 was performed.

<<example 6>> Changed the photosensitive diazo quinone compound B-1 in the photopolymer constituent in an example 1 to B-3, further, the addition of this component was changed, as shown in a table 1, and also the same assessment as an example 1 was performed.

<<example 7>> The addition of the photosensitive diazo quinone compound B-1 in the photopolymer constituent in an example 1 was changed as shown in a table 1, and also the same assessment as an example 1 was performed.

[0059] Example of <<comparison 1>> 3, 3', and after suspending 4 and 322.2g (1.0 mols) of 4'-benzophenone tetracarboxylic dianhydride in the N-methyl-2-pyrrolidone and dissolving thoroughly, para xylene -2 and 129.4g (0.95 mols) of 5-diamines were added, and the reaction was performed at 30 degrees C for 18 hours. The reactant was reprecipitated with the methanol, the solid was condensed, with the methanol, after washing, reduced pressure drying was carried out for 48 hours, and the target polyamide (A-5) was compounded. Others performed the same assessment as an example 1.

Example of <<comparison 2>> Changed the photosensitive diazo quinone compound B-1 in the photopolymer constituent in an example 1 to B-4, further, the addition of this component was changed, as shown in a table 1, and also the same assessment as an example 1 was performed.

Example of <<comparison 3>> Changed the photosensitive diazo quinone compound B-1 in the photopolymer constituent in an example 1 to B-5, further, the addition of this component was changed, as shown in a table 1, and also the same assessment as an example 1 was performed.

Example of <<comparison 4>> Changed the photosensitive diazo quinone compound B-1 in the photopolymer constituent in an example 1 to B-6, further, the addition of this component was changed, as shown in a table 1, and also the same assessment as an example 1 was performed.

Example of <<comparison 5>> The addition of the photosensitive diazo quinone compound B-1 in the photopolymer constituent in an example 2 was changed as shown in a table 1, and also the same assessment as an example 1 was performed.

Example of <<comparison 6>> The addition of the photosensitive diazo quinone compound B-1 in the photopolymer constituent in an example 2 was changed as shown in a table 1, and also the same assessment as an example 1 was performed. The assessment result of examples 1-7 and the examples 1-6 of a comparison is shown in a table 1.

[0060]

[A table 1]

表 1

	ホリミド (A) (g)	感光性 ジアゾキノ (B) (g)	感度 (mJ/cm ²)	残膜率 (%)
実施例1	A-1 100	B-1 25	230	93.1
実施例2	A-2 100	B-1 25	210	91.0
実施例3	A-3 100	B-1 25	230	91.5
実施例4	A-4 100	B-1 25	210	89.7
実施例5	A-1 100	B-2 35	220	92.3
実施例6	A-1 100	B-3 30	240	93.8
実施例7	A-1 100	B-1 15	190	86.8
比較例1	A-5 100	B-1 25	240	71.3
比較例2	A-1 100	B-4 30	350	90.1
比較例3	A-1 100	B-5 30	410	92.0
比較例4	A-1 100	B-6 30	330	86.7
比較例5	A-2 100	B-1 0.5	<50	1.5
比較例6	A-2 100	B-1 120	540<	99.7

[0061] <<example 8>> 6g (C-1) of bisphenol compounds which have the structure of the following type, and 6g (D-1) of tris phenolic compounds which have the structure of the following type were added to the photopolymer constituent in an example 1, and the same assessment as an example 1 was performed. The sensitivity at this time showed the value with both as high 190 mJ/cm² and remaining rates of membrane as 91.5%. Next, make this positive type photopolymer constituent be the same as that of an example 1. It applied on the silicon wafer, and after prebaking, heating and resin were stiffened in order (30 minutes in oven / 150 degrees C, 30 minutes / 250 degrees C, and 30 minutes / 350 degrees C), and the epoxy resin constituent for semiconductor closure (the Sumitomo Bakelite Co., Ltd. make, EME-6300H) was fabricated on this hardening film the back in magnitude of 2x2x2mm (horizontal x length x height). As a result of measuring the shear strength of the epoxy resin constituent for closure fabricated on the poly benzo oxazole resin hardening film using tensilon, 3.7kg / was [mm] 2.

[0062] Next, after applying this positive type photopolymer constituent to the simulation element wafer which equipped the front face with aluminum circuit so that it may become with the 5 micrometers of

the last thickness, last BEKU of the pattern processing was performed and carried out. It divided for every chip size after that, and after using and mounting a conductive paste on the leadframe for 16Pin DIP (Dual Inline Package), it closed with the epoxy resin for semiconductor closure (the Sumitomo Bakelite Co., Ltd. make, EME-6300H), and the semiconductor device was obtained. After processing 20 semiconductor devices under the conditions of 85 degrees C / 85% humidity for 168 hours, although it was immersed in 260-degree-C solder organ bath for 10 seconds and an elevated temperature and highly humid pressure cooker processing (125 degrees C, 2.3atm, 100%RH) were subsequently performed for 1 000 hours, poor opening of aluminum circuit was 0.

* The positive type photopolymer constituent put into the bottle of 100ml of shelf-life stability assessment and dry ice 10kg were put into the box of firing styrol, and it covered, sealed as it is and put into the -20--15 degree C freezer for one week further after neglect neglect for five days. However, there was no sludge etc. into a positive type photopolymer constituent, and conservation stability was good. <<example 9>> From A-1, changed the photosensitive diazo quinone to B-2 from B-1, and changed the bisphenol compound C-1 for the polyamide in an example 8 to C-2 A-2, further, the addition of each component was changed, as shown in a table 2, and also the same assessment as an example 8 was performed.

<<example 10>> Changed the tris phenolic compound D-1 in an example 8 to D-2, further, the addition of each component was changed, as shown in a table 2, and also the same assessment as an example 8 was performed.

[0063] Example of <<comparison 7>> Changed the bisphenol compound C-2 in an example 9 to C-3, further, the addition of each component was changed, as shown in a table 2, and also the same assessment as an example 8 was performed.

Example of <<comparison 8>> Changed the tris phenolic compound D-1 in an example 8 to D-3, further, the addition of this component was changed, as shown in a table 2, and also the same assessment as an example 8 was performed.

Example of <<comparison 9>> Set the addition of the bisphenol compound C-2 in an example 9 to 30g, and set the addition of the tris phenolic compound D-1 to 15g, further, the addition of each component was changed, as shown in a table 2, and also the same assessment as an example 8 was performed.

Example of <<comparison 10>> Set the addition of the bisphenol compound C-1 in an example 8 to 0.2g, and set the addition of the tris phenolic compound D-1 to 0.2, further, the addition of each component was changed, as shown in a table 2, and also the same assessment as an example 8 was performed.

Example of <<comparison 11>> Set the addition of the bisphenol compound C-2 in an example 9 to 0g, and set the addition of the tris phenolic compound D-1 to 18g, further, the addition of each component was changed, as shown in a table 2, and also the same assessment as an example 8 was performed.

Example of <<comparison 12>> Set the addition of the bisphenol compound C-2 in an example 9 to 20g, and set the addition of the tris phenolic compound D-1 to 0g, further, the addition of each component was changed, as shown in a table 2, and also the same assessment as an example 8 was performed. The assessment result of examples 8-10 and the examples 7-12 of a comparison is shown in a table 2 above.

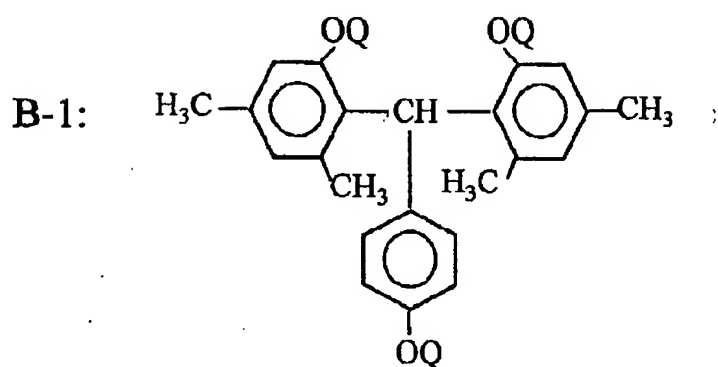
[0064]

[A table 2]

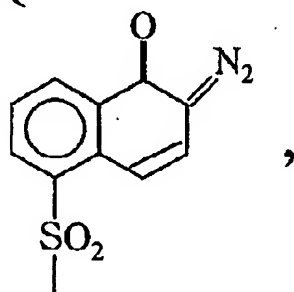
表 2

	モノリシック (A) (g)	感光性 レジスト (B) (g)	ヒステリシス (C) (g)	トリスリシス (D) (g)	感度 (mJ/cm ²)	残膜率 (%)	保存性	せん断 密着強度 (kg/mm ²)	半導体の信頼性 (不良数/20A ² パージ)	
									PCT 500hrs	PCT 1000hrs
実施例8	A-1 100	B-1 25	C-1 6	D-1 6	190	91.5	析出無し	3.7	0/20	0/20
実施例9	A-2 100	B-2 25	C-2 10	D-1 6	180	90.8	析出無し	3.6	0/20	0/20
実施例10	A-1 100	B-1 30	C-1 8	D-2 9	190	91.7	析出無し	3.5	0/20	0/20
比較例7	A-2 100	B-2 30	C-3 8	D-1 6	130	72.2	析出無し	3.0	0/20	0/20
比較例8	A-1 100	B-1 25	C-1 6	D-3 10	240	92.7	析出無し	3.4	0/20	0/20
比較例9	A-2 100	B-2 30	C-2 30	D-1 15	150	80.1	析出有り	3.2	0/20	0/20
比較例10	A-1 100	B-1 30	C-1 0.2	D-1 0.2	280	94.3	析出無し	1.9	1/20	9/20
比較例11	A-2 100	B-2 30	C-2 0	D-1 18	140	77.2	析出無し	3.8	0/20	0/20
比較例12	A-2 100	B-2 25	C-2 20	D-1 0	170	89.9	析出有り	3.7	0/20	0/20

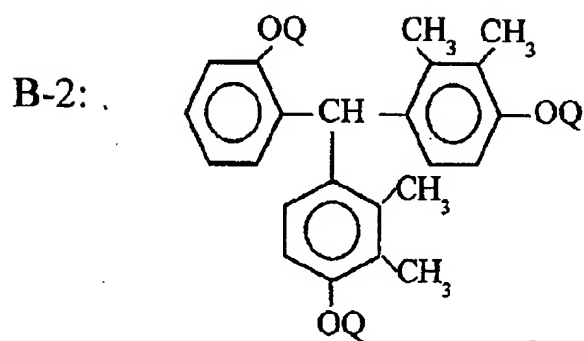
[0065]



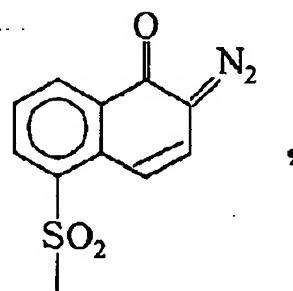
(式中の Qの70%が



Qの30%が 水素原子 である)



(式中の Qの55%が



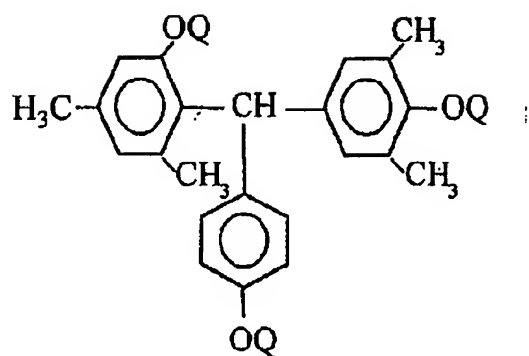
Qの45%が 水素原子 である)

[Formula 39]

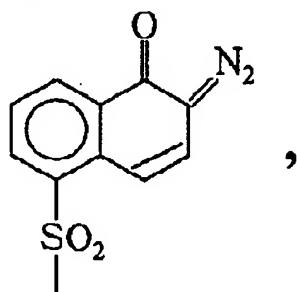
[0066]

[Formula 40]

B-3:

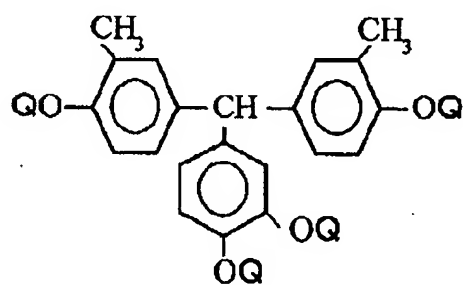


(式中の Qの60%が

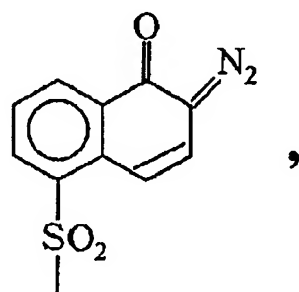


Qの40%が 水素原子 である)

B-4:



(式中の Qの60%が

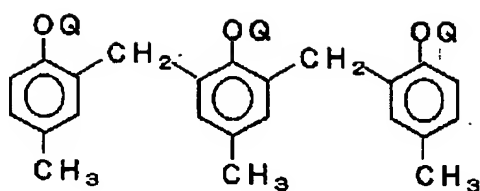


Qの40%が 水素原子 である)

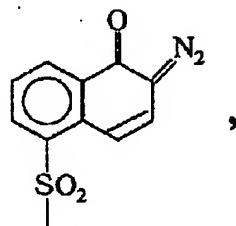
[0067]

[Formula 41]

B-5:

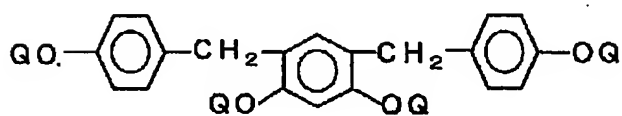


(式中の Qの70%が

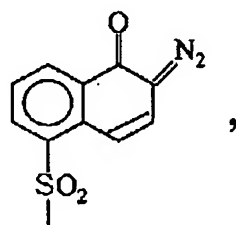


Qの30%が 水素原子 である)

B-6:



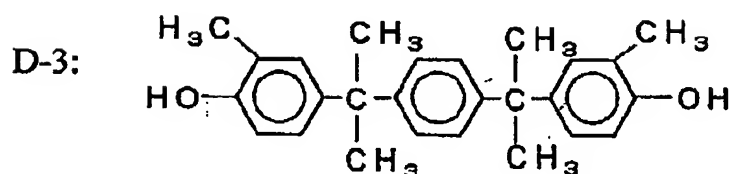
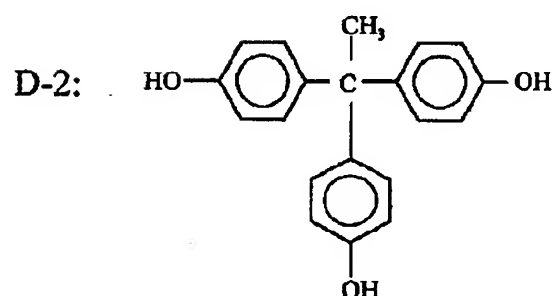
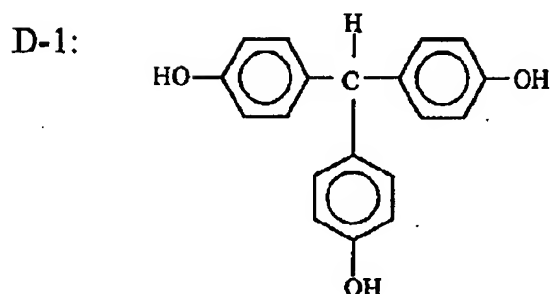
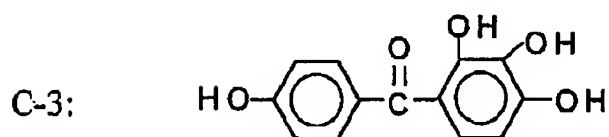
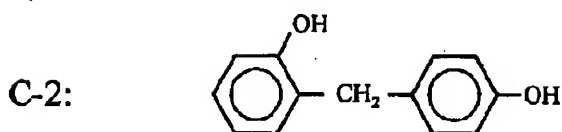
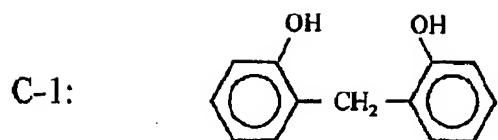
(式中の Qの55%が



Qの45%が 水素原子 である)

[0068]

[Formula 42]



[0069] * Both the assessment result examples 1-4 and the example 1 of a comparison are assessment by the presentation of only a polyamide and a photosensitive diazo quinone (B-1). Although both examples showed comparable sensitivity, in the case of the polyimide precursor (A-5) of the example 1 of a comparison, the remaining rate of membrane fell substantially compared with the poly benzo oxazole precursor (A-1-4). This is considered that a cause is in the interaction of base resin and a sensitization

agent. It is in the inclination for electron density to become high at the non-replaced para position, to the hydroxyl group in B-1. In the examples 1-4, when the hydroxyl group which exists in A-1-4 carries out hydrogen bond to the para position in the high electron density in B-1, since base resin fully received the lysis inhibition effect by the sensitization agent, it is thought that the high remaining rate of membrane was shown. However, by A-5 in which a hydroxyl group does not exist, since an interaction with a sensitization agent becomes weak, it is thought that the remaining rate of membrane fell. Examples 1, 5, and 6 and the examples 2-4 of a comparison are assessment by the class of photosensitive diazo quinone. The examples 2-4 of a comparison which use the photosensitive diazo quinone which a sensitization radical is not uniformly arranged moderately and does not have the non-replaced para position show low sensitivity, and are not comparatively [the] high. [of a remaining rate of membrane] The cause of low sensitivity is considered for nonuniformity to arise in the solubility in the exposure section at the time of development. Examples 1 and 7 and the examples 5 and 6 of a comparison are assessment by the amount of a photosensitive diazo quinone. In order that the lysis inhibition effect may not commit the example 5 of a comparison whose addition is under 1 weight section, the remaining rate of membrane is falling remarkably, rather than the 100 weight sections, in many examples 6 of a comparison, the lysis inhibition effect is too strong conversely, and sensitivity is falling substantially. Examples 8-10 and the examples 7-12 of a comparison are assessment by the class and amount of a bisphenol compound and a tris phenolic compound. ** in which, as for the example 7 of a comparison which replaced the class of bisphenol compound with, high sensitivity-ization is accepted -- the remarkable decline in a remaining rate of membrane is seen. In the example 8 of a comparison which replaced the class of tris phenolic compound with, a result of low sensitivity and a high remaining rate of membrane is brought conversely. In the example 9 of a comparison with more additions of both phenolic compounds than 30 weight sections, by the example 10 of a comparison which is under 1 weight section, a deposit is produced in the conservation at the time of refrigeration in lowering and coincidence of a remaining rate of membrane, and while sensitivity falls, adhesion with closure resin falls, and the reliability of a semiconductor device is also falling. the example 11 of a comparison which is the presentation of only a tris phenolic compound -- the example 7 of a comparison -- the same -- the degree of high feeling -- also becoming -- decline in a large remaining rate of membrane can be checked. Although the example 12 of a comparison which is the presentation of only a bisphenol compound shows high sensitivity and a high remaining rate of membrane, it has produced the deposit at the time of frozen conservation.

[0070]

[Effect of the Invention] according to this invention -- high sensitivity -- high -- a remaining rate of membrane pattern can obtain the highly reliable semiconductor device using the positive type photopolymer constituent and it which are excellent in adhesion with **** and closure resin, and conservation stability.

[Translation done.]